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Measurement of Aerodynamic Shear Stress
Using Side Chain Liquid Crystal Polymers

by Carlo Greg N. Demandante, Captain, USAF

A sixty page thesis submitted in partial
fulfillment of the requirements for the degree of
Master of Science, University of Washington, 1992

Chairperson of the
Supervisory Committee: Professor Martin P. Gouterman
Department of Chemistry

Abstract

A novel concept was proposed exploiting the optical property response of liquid crystalline materials to various external effects. This study determined the feasibility of using side chain liquid crystal polymers as aerodynamic shear sensors. A method was developed to observe and measure the optical birefringent response of film coatings made from these polymer materials due to applied shear. Different polymers were synthesized, spray-coated and tested for their shear-sensing potential. Empirical results confirmed the promise of this method on future aerodynamic testing.

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- H. Finkelman, H.-J. Kock and G. Rehage, Makromol. Chem., Rapid Commun., 2, 317, (1981).
- H. Ringsdorf and A. Schneller, Makromol. Chem., Rapid Commun., 3, 557, (1982).
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Carlo Greg N. Demandante

A thesis submitted in partial fulfillment
of the requirements for the degree of

Master of Science

University of Washington

1992

Approved by Martin Gonterman
Chairperson of Supervisory Committee


Program Authorized
to Offer Degree CHEMISTRY

Date May 29, 1992

Master's Thesis

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May 29, 1992

University of Washington

Abstract

Measurement of Aerodynamic Shear Stress
Using Side Chain Liquid Crystal Polymers

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GLOSSARY

dp	Degree of polymerization
IR	Infrared absorption
LC	Liquid crystal
LCC	Liquid crystal copolymer
LCP	Liquid crystal polymer
LCP 525	LCP synthesized with the Crosslinker 525 PDMSHMS polymer
LCP X-63	LCP synthesized with the Silicone Fluid X-63 PDMSHMS polymer
OD	Filter optical density
PDMSHMS	Poly(dimethylsiloxane-co-hydrogenmethyl siloxane) polymer
S/N ratio	Ratio of signal to noise
T_g	Glass phase transition temperature
T_i	LC clearing temperature
THF	Tetrahydrofuran solvent
"wind-off"	Condition where no shear stress is applied to a sample plate
"wind-on"	Condition where shear stress is applied to a sample plate by blowing gas horizontally over the surface
X:Y ratio	Ratio of the dimethylsiloxane unit to the hydrogenmethylsiloxane unit in a PDMSHMS polymer

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*To Tatay and Nanay, for their caring guidance
and steadfast encouragement through the years*

*Erst die Theorie entscheidet darüber,
was beobachtet werden kann*

-- Albert Einstein

Chapter 1. Introduction

1.1 Liquid Crystal Theory

Liquid crystals (LCs) were first observed in 1888 by Friedrich Reinitzer. The liquid crystalline state, lying between the crystalline and the isotropic liquid states of matter, offers a broad range of applications where its anisotropic but liquid properties can be exploited for sensing the environment. The weak forces between LC molecules are easily disturbed by various external effects producing marked changes in its optical properties such as reflection, transmission, dichroism, birefringence and color.¹ Application of mechanical stress, for example, will reorient the LC structure and, thereby, change its birefringent property; this characteristic makes these materials ideal shear sensors.

Conventional, non-LC methods of studying boundary layer behavior such as oil films or Preston tubes are either difficult to interpret or only provide local measurements of shear stress.² In 1968, Enrique J. Klein introduced the use of LC in aerodynamic testing³ and, despite some drawbacks, it has proven a very promising boundary layer sensor.^{4,5}

In LC shear-sensing, the observed reflection spectra are also difficult to interpret. Adding to the problem, the

thickness of the LC film during the testing is difficult to maintain due to the hydrodynamic and kinetic effects caused by the applied shear. Finally, current LC sensors are relatively slow compared to the rapidly changing flow patterns.^{4,5}

D.S. Parmar of NASA Langley is working on the interpretation and response time problem by measuring the change in birefringence and working with ferroelectric LCs⁴; the hydrodynamic flow, however, remains a problem. One possible solution is to attach these LC structures to a matrix which inhibits their movement while still allowing them to retain their high degree of orientation and sensitivity, i.e., liquid crystal polymers.

1.2 Liquid Crystal Polymers (LCPs)

LCPs are high molar mass materials which exhibit liquid crystalline behavior. Although most of the recent interest in LCP materials are due to its inherent physical properties including high strength and stiffness over a broad range of temperature, there is also great interest in the material for its potential in the fields of application currently using low molar mass LCs.⁶

LCPs can be tailored for the best combination of properties deriving from the anisotropic behavior of LCs and

the polymer-specific characteristics of macromolecules. Two basically different types of LCPs are conceivable: the mesogenic groups form the polymer main chain (main chain LCPs), or the mesogenic groups are attached as side chains to the monomer unit of the polymer backbone (side chain LCPs) (Fig. 1). This study will focus on the latter since they offer field effects and optical properties more similar to low molar mass LCs.⁷

1.3 Polarized Fluorescence

Optical anisotropy, such as birefringence and dichroism, of oriented polymers has been utilized for the measurement of molecular orientation. Another method involves the use of the polarized fluorescence emitted from probes dispersed within the polymer. This method provides greater insight into the distribution of molecular orientations labeled by the probe molecules. Polarized fluorescence can measure not only the static orientation of the molecule but also any dynamic process such as reorientation.^{8,9,10} It becomes possible to observe a polymer orientation transformation process, e.g., LCP structural deformation due to shear application.

Helmut Ringsdorf has successfully attached dyes to LCPs, thereby, creating liquid crystal copolymers (LCCs)

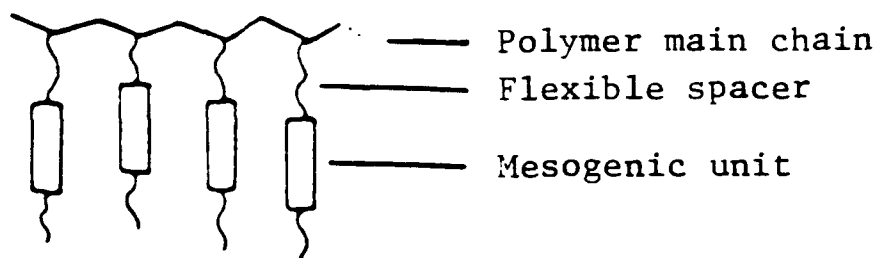


Figure 1. Schematic structure of side chain LCP; flexible spacers decouple the orientation of mesogenic side groups from any polymer main chain effects

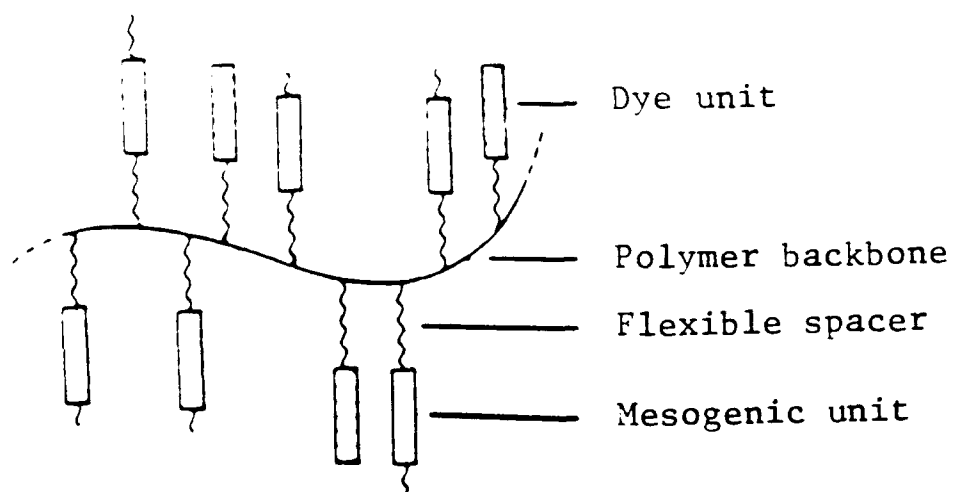


Figure 2. Schematic structure of LCC with dye and mesogenic side groups

with dyes and mesogens as side groups (Fig. 2). Results showed no drastic change in liquid crystalline behavior at low dye concentrations.^{11,12} Although these studies involved the use of dichroic and pleochroic dyes to improve the LCC optical display, it should also be possible to covalently attach fluorescent dyes and use them as probes to study the LCC orientation.

1.4 Research Objectives

The long range goal of this research is the development of a method to map the shear stress distribution on the surface of an airfoil. This thesis is an initial concept study to determine the feasibility of LCPs as shear sensors. The study aimed to meet the following objectives:

1. Syntheses and surface application of LCPs as film coatings for shear-sensing.
2. Construction of a testing apparatus for current and future shear-sensing coating studies.
3. Development of a methodology to observe and measure the optical birefringent response from the LCP coatings.
4. Confirmation of the shear-sensing concept from the optical response of the LCP films due to applied shear.

Chapter 2. Side Chain Liquid Crystal Polymer

LCPs are a new class of thermoplastics providing an outstanding balance of properties for high performance applications. Due to its high molecular orientation, the material is characterized by high stiffness and strength, broad chemical resistance and thermal stability.^{13,14} However, for this research application, the LCP needed to show a liquid crystalline phase at low temperatures; the glass phase transition (T_g) must be low, and the liquid crystalline phase needed to cover the aerodynamic testing range.

2.1 Variation in Phase Transition (T_g)

T_g is the lower temperature limit of the liquid crystalline phase; it is the phase transition temperature from a crystalline (solid) to a liquid crystalline phase. Transition from the liquid crystalline to an isotropic liquid phase occurs at the clearing temperature, T_i .¹⁵

The T_g of most LCPs is too high to prepare and observe a stable liquid crystalline phase. Finkelmann and Ringsdorf have noted factors which influence phase behavior of LCPs. Lowering of T_g is possible by attaching the mesogenic groups

to a flexible backbone^{16,17} and/or by reducing the interaction between the mesogenic side groups through the introduction of additional spacers in the main chain.^{17,18,19}

2.2 Polyacrylic and Polysiloxanic LCPs

Helmut Ringsdorf was successful in synthesizing a polyacrylic LCP with low T_g , -10°C .¹¹ The LCP was prepared by free radical polymerization of the mesogenic monomer, 6-acryloyl oxyhexyl 4-(trans-4-propylcyclohexyl)benzoate. As mentioned earlier, he then went on to synthesize copolymers of mesogenic and dye monomers which still retained a relatively low T_g .^{11,12} This should prove particularly important in the proposed follow-on studies on polarized fluorescence where fluorescent dyes are covalently attached to the LCP (section 5.2).

However, this research focused on polysiloxanic LCPs. The synthesis and characterization, initially investigated by Heino Finkelmann^{16,18} and continued by Ringsdorf¹⁹, involved polymer modification of the poly(dimethylsiloxane-co-hydrogenmethylsiloxane) (PDMSHMS) polymer. The LCP is prepared by a polyhydrosilation reaction of the polymer with a terminal alkenic mesogenic side chain, in this case, 4-(3-butenyloxy)benzoic acid 4'-methoxyphenyl ester (Fig. 3).

For a degree of polymerization (dp) of 120 ($X+Y=120$) and an X:Y ratio of 1:1 ($X=Y=60$), this LCP has a smectic liquid crystalline phase of -6°C to 50°C .¹⁸ For this research the LCPs synthesized also had dps of 120 but X:Y ratios of only 2.5:1 or 2:1 making them less viscous films with even lower T_g s.

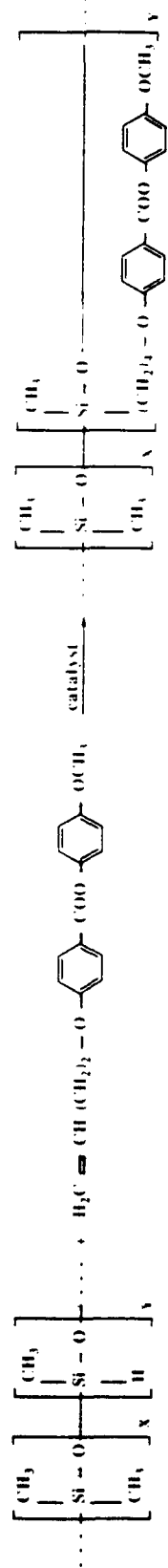


Figure 3. Polyhydrosilation reaction for LCP synthesis; the PDMSHMS polymer is not a block copolymer; the copolymers units are randomly distributed within the polymer chain

Chapter 3. Experimental

The mesogenic side chain alkenes used in this research, 4-(3-butenyloxy)benzoic acid 4'-methoxyphenyl ester, were prepared by Frinton Laboratories, Inc. using standard methods published in the literature.^{16,18}

The PDMSHMS polymers were provided by Wacker Silicones Corporation. Crosslinker 525 is a pure PDMSHMS polymer with a dp of 120 and an X:Y ratio of 2.5:1.²⁰ Silicone Fluid X-63 is a formulated product with a dp of 120, an X:Y ratio of 2:1 and a 1.4% methylvinylsiloxane polymer unit within the polymer chain. It also has an octamethylcyclotetra-siloxane component in the polymer solution at 5 ppm.²⁰ LCPs synthesized with Crosslinker 525 and Silicone Fluid X-63 are, henceforth, designated LCP 525 and LCP X-63, respectively (Fig. 4).

3.1 LCP 525 Synthesis

To a mixture of PDMSHMS (Crosslinker 525, 0.91 g) and a 10% molar excess of the side chain alkene (1.1 g) in tetrahydrofuran (THF, 5 ml), H_2PtCl_6 catalyst was added at 100 ppm. The solution was heated under reflux for 18.5 hours at 55°C. After complete addition (disappearance of

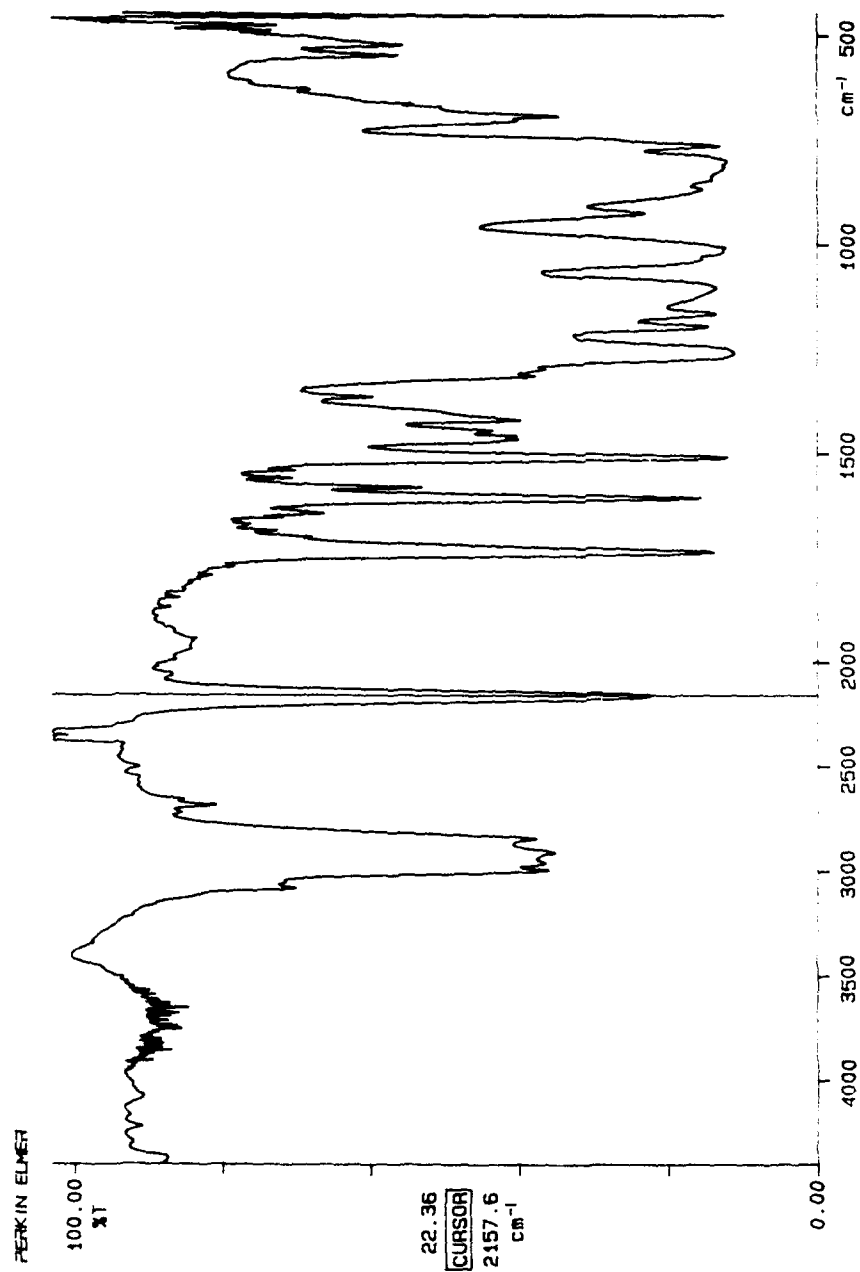
the Si-H absorption peak at 2158 cm^{-1} , Figs. 5 and 6), the LCP was isolated by precipitation with methanol. The LCP precipitant was then purified over night by soxhlet extraction using a methanol solvent.

3.2 Octenyl Polysiloxane Synthesis

To verify the inherence of shear response behavior only to side chain LCPs, a control side chain polymer was also synthesized. Addition of 1-octene to the polysiloxane (1 g PDMSHMS, 1.02 g 1-octene) was carried out in the same procedure as the LCP 525 synthesis. The final product was a poly(dimethylsiloxane-co-methyloctenylsiloxane) polymer with the same dp and X:Y ratio as LCP 525 (Fig. 4).

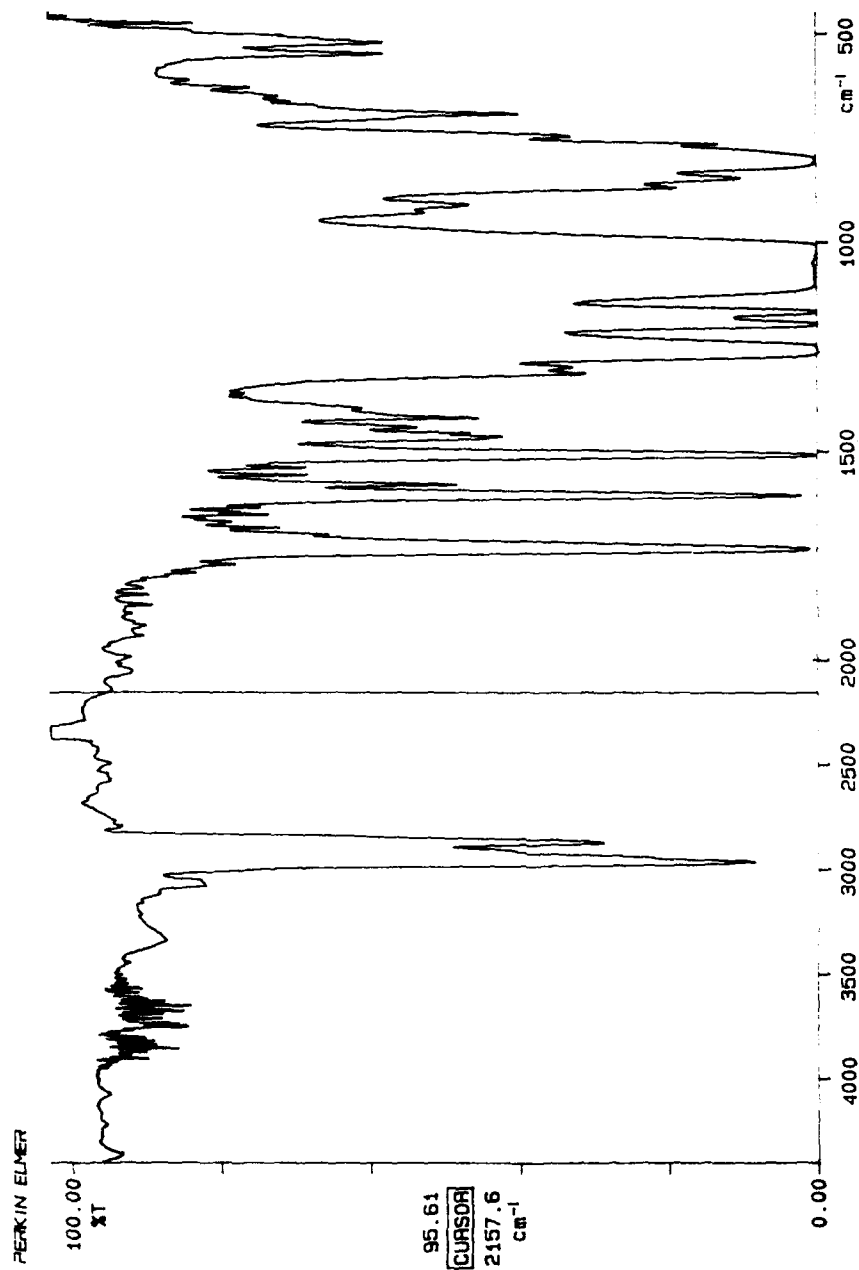
3.3 LCP X-63 Synthesis

This polymer was synthesized to determine the relationship between LCP shear response and its viscosity. LCP X-63, with a lower X:Y ratio, should prove more viscous than LCP 525; there is less spacing between the mesogenic side chains inducing more interaction and, thereby, higher viscosity.



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lcp61: 4 scans, 4.0cm⁻¹
before reflux

Figure 5. IR spectrum before hydrosilation in LCP 525 synthesis;
Si-H stretch absorption at 2158 cm⁻¹



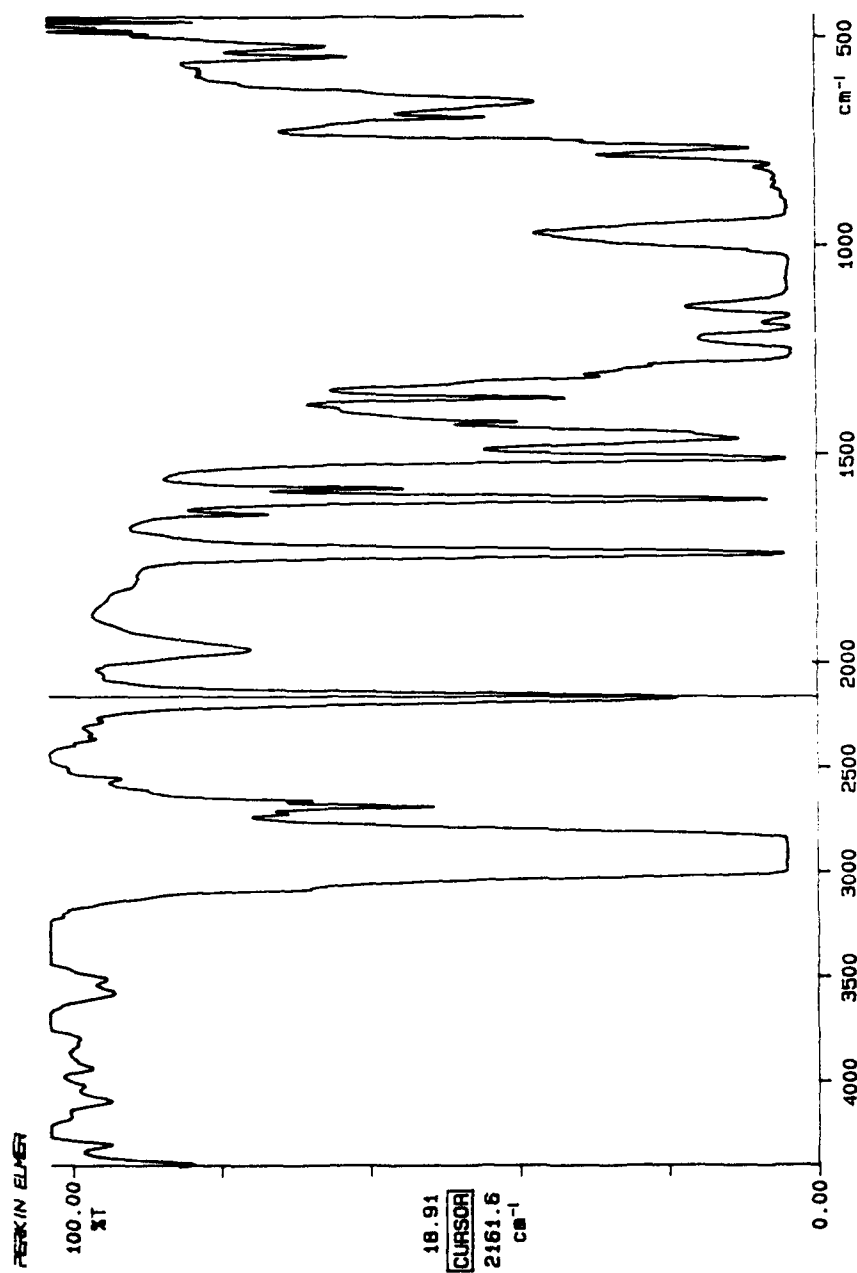
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lcp63: 4 scans, 4.0cm⁻¹
reflux 18.5 hrs

Figure 6. IR spectrum after hydrosilation in LCP 525 synthesis;
disappearance of Si-H stretch absorption

Addition of the side chain alkene (1.01 g) to the PDMSHMS (Silicone Fluid X-63, 0.72 g) in 10 ml THF was initially carried out in the same procedure as the LCP 525 synthesis. However, gel byproducts formed during reflux. This was most likely due to a hydrosilation crosslinking of the polymer through the methylvinylsiloxane unit. The addition reaction also did not go forward completely; a residual Si-H absorption remained in the IR spectrum and did not diminish on further heating (Figs. 7, 8 and 9). After 19.5 hours of reflux, 1-octene was added to mop up the remaining Si-H and the solution was left to reflux for another 4.5 hours. Previous studies have revealed no differences in physical properties for polymers made with and without 1-octene.²¹ After complete addition (Fig. 10), the LCP in solution was separated from the gel byproducts. The LCP was then isolated and purified by repeated precipitation with methanol.

3.4 Instrumentation

The testing apparatus is shown schematically in Fig. 11. The light source is a 150 watt Xenon arc lamp (Model 6137, Oriel Corp.). The focusing lenses (focal lengths 2.7 and 3) are adjusted to collimate the light through the crossed polarizers (03 FPG 007, Melles



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lcp81: 4 scans, 4.0cm⁻¹
before reflux

Figure 7. IR spectrum before hydrosilation in LCP X-63 synthesis;
Si-H stretch absorption at 2162 cm⁻¹

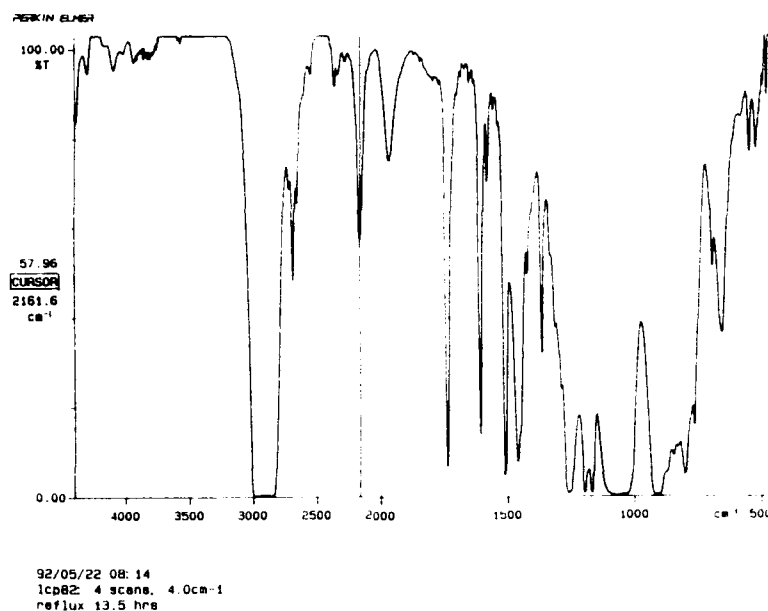


Figure 8. IR spectrum after 13.5 hours reflux; LCP X-63 synthesis

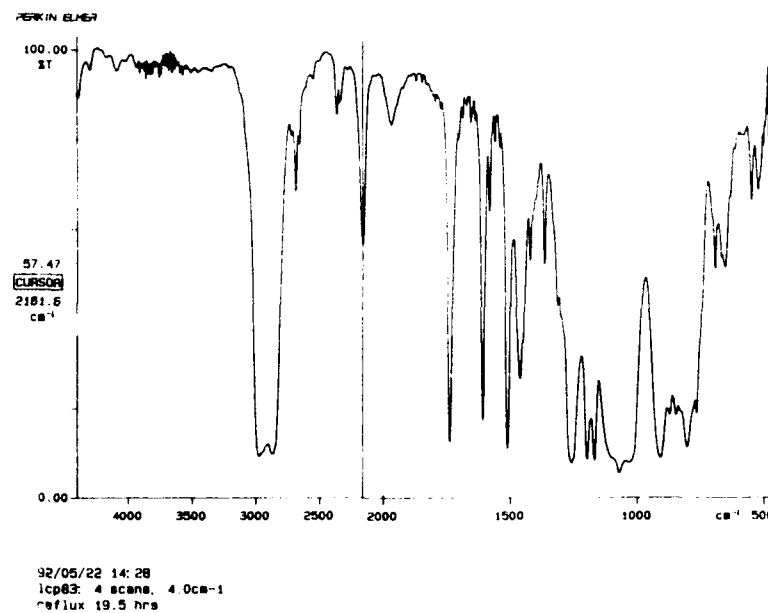
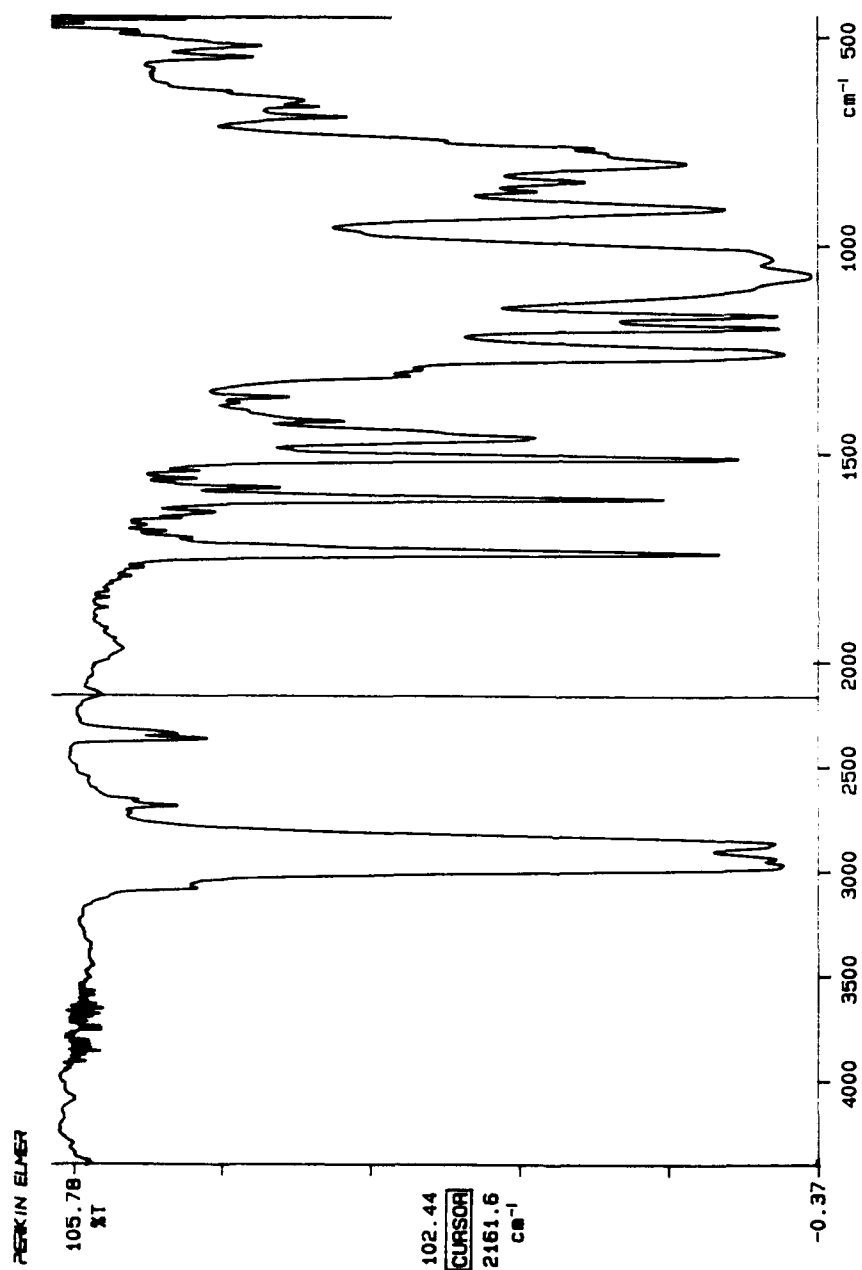


Figure 9. IR spectrum after 19.5 hours reflux; LCP X-63 synthesis



92/05/22 18:10
lcp84: 4 scans, 4.0cm⁻¹
1.octene added; reflux 24 hrs total

Figure 10. IR spectrum after hydrosilation in LCP X-63 synthesis;
1-octene added; total 24 hours reflux

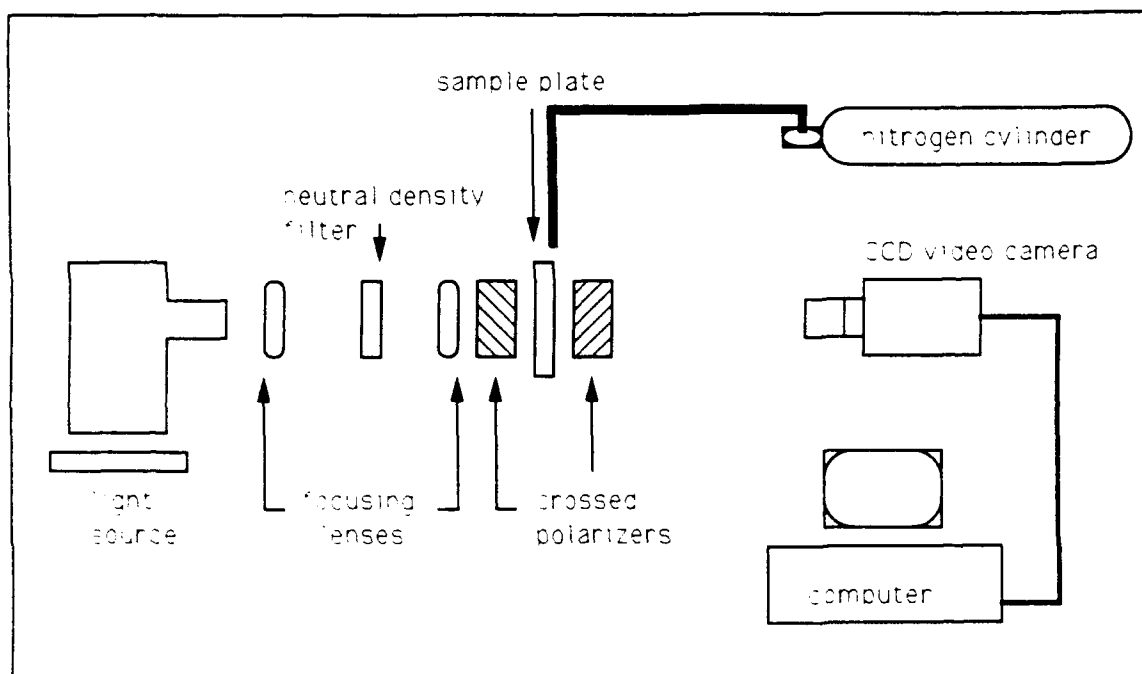


Figure 11. Schematic diagram of the experimental setup

Griot), sample plate and video camera. Neutral density filters are added to prevent light saturation of the video camera. The camera is a Sony XC-77RR CCD video camera system fitted with a 50 mm television lens (Cosmicar, focal length 1.4) and a 20 mm extension for close-up work. Video images are captured and processed in an Apple Macintosh IIX computer using the IPLab Scientific Image Processing software (Signal Analytics Corp.).

3.4 Testing Procedure

The purified LCP is redissolved in THF in different percent weight ratios. The LCP solution is spray-coated on a flat glass surface and left to dry. The dried sample plate is placed between crossed polarizers and illuminated. Nitrogen gas from a cylinder is blown horizontally over the plate surface (henceforth designated as a "wind-on" condition). Being birefringent, the LCP will affect the optical polarization of the incident light. Any molecular reorientation of the LCP due to the applied shear can be observed optically by monitoring the change in polarization of the transmitted light.

The amount of shear stress applied on the surface could not really be quantified with this experimental setup; however, a calibration setup is possible and suggested as a

follow-on study (section 5.2). The initial flow pressure from the cylinder is approximately 15 psi but drastically increases as it flows through the compressed pipette nozzle. Applied shear is also dependent on the nozzle placement relative to the plate surface.

Video images of a "wind-on" and a "wind-off" conditions are captured and processed. The difference between the images is analyzed and any change correlates to the change in polarization caused by the LCP coating response to the applied shear. A signal-to-noise (S/N) ratio is then calculated using the gray scale values in the image difference. Another "wind-off" image is taken after the shear application. The difference between the two "wind-off" images correlates to a permanent reorientation/deformation of the LCP coating due to the applied shear. Any deformation is detrimental to future calibration of shear response; this would be similar to the spectral interpretation problem of low molar mass LCs due to thinning.

Chapter 4. Results and Discussion

4.1 Infrared (IR) Spectra

IR spectroscopy was the analytical method selected for monitoring the polyhydrosilation reaction and confirming the structure of the different polymer materials. Each material was dissolved in THF in similar percent weight ratios. The IR spectra were taken with a Perkin Elmer Model 1600 FT-IR Spectrophotometer. Assignment of the absorption peaks were based on the characteristic bond vibrations of linear polysiloxanes.^{22,23}

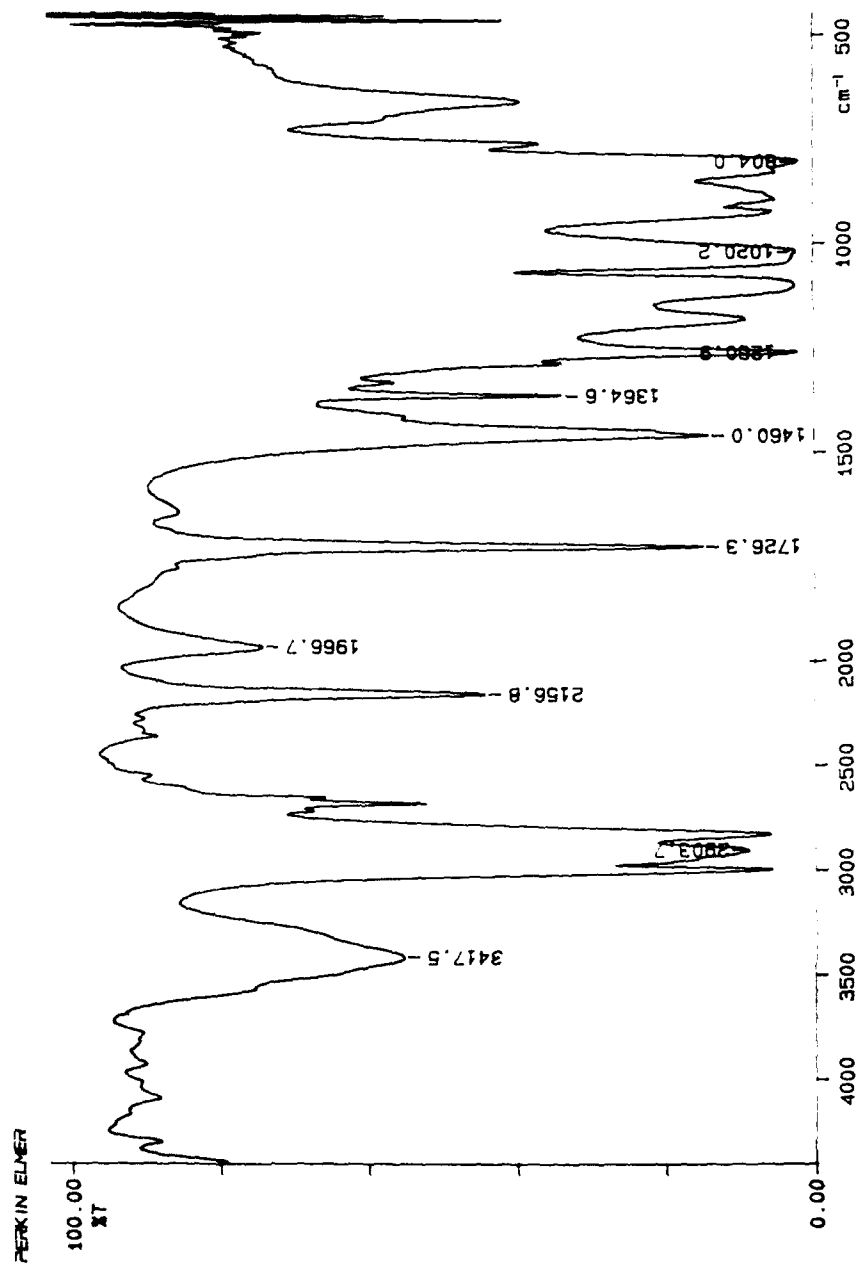
4.1.1 PDMSHMS Polymer (Crosslinker 525)

The IR spectrum of the unreacted polysiloxane polymer (Fig. 12) confirms its structure. The broad peak around 3420 cm^{-1} is an H_2O impurity. As it turns out, the impurities present in all the polymer solutions came from the stock THF solvent; this is fully explained in section 4.1.4. The peaks around 2900 cm^{-1} are due to the asymmetric and symmetric C-H stretches. The sharp peak at 2157 cm^{-1} is the distinctive Si-H stretch peak. This peak is used to monitor the polyhydrosilation reaction during the LCP

synthesis. The peaks at 1460 cm^{-1} and around 1365 cm^{-1} are due to the CH_3 asymmetric and symmetric bending, respectively. The sharp peak at 1261 cm^{-1} is the Si- CH_3 rock. The broad peaks around 1020 cm^{-1} and 804 cm^{-1} are from the Si-O stretch and Si-C stretch, respectively.

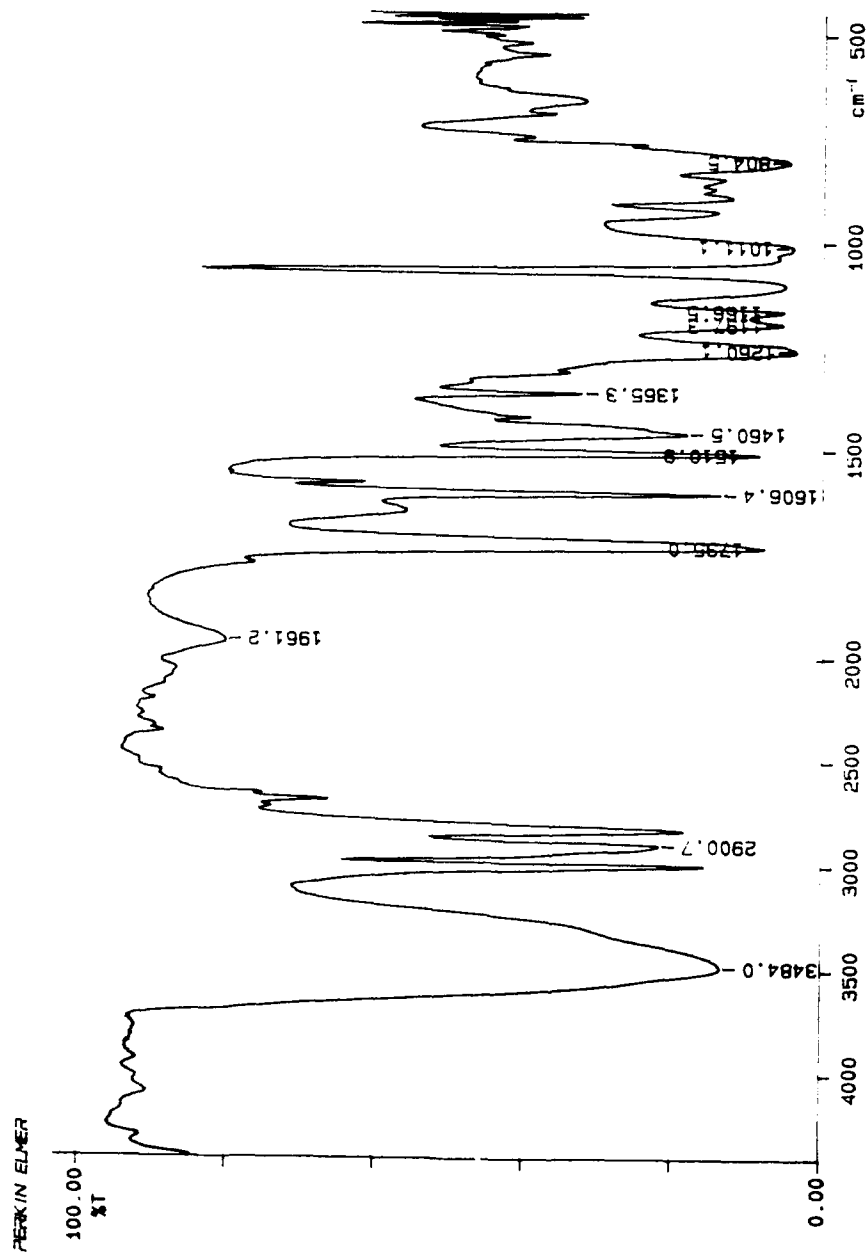
4.1.2 LCP 525

Addition of the LC side chain to the Crosslinker 525 polymer gives a somewhat similar IR spectrum (Fig. 13). The bigger and broader O-H stretch peak is most likely due to water retention during the reflux and methanol residuals from the soxhlet extraction. The Si-H peak at 2157 cm^{-1} has disappeared, confirming complete hydrosilation. In addition to the same peaks present in the polysiloxane spectra, the LCP spectra also shows an aromatic ring stretch pair at 1606 cm^{-1} and 1511 cm^{-1} . The C-O stretch also occurs in pair at 1197 cm^{-1} and 1166 cm^{-1} . The strong peak at 1735 cm^{-1} is due to the C=O stretch and an impurity which is explained in section 4.1.4. These peaks confirm the addition of the LC side chain to the polysiloxane polymer.



92/05/09 14:38
polymer: 4 scans, 4.0cm⁻¹
polysiloxane\thf; 5.02% wt

Figure 12. IR spectrum of the Crosslinker 525 polymer



92/05/09 15:08
lcp6: 4 scans, 4.0cm-1
lcp6\thf: 4.79% wt

Figure 13. IR spectrum of LCP 525

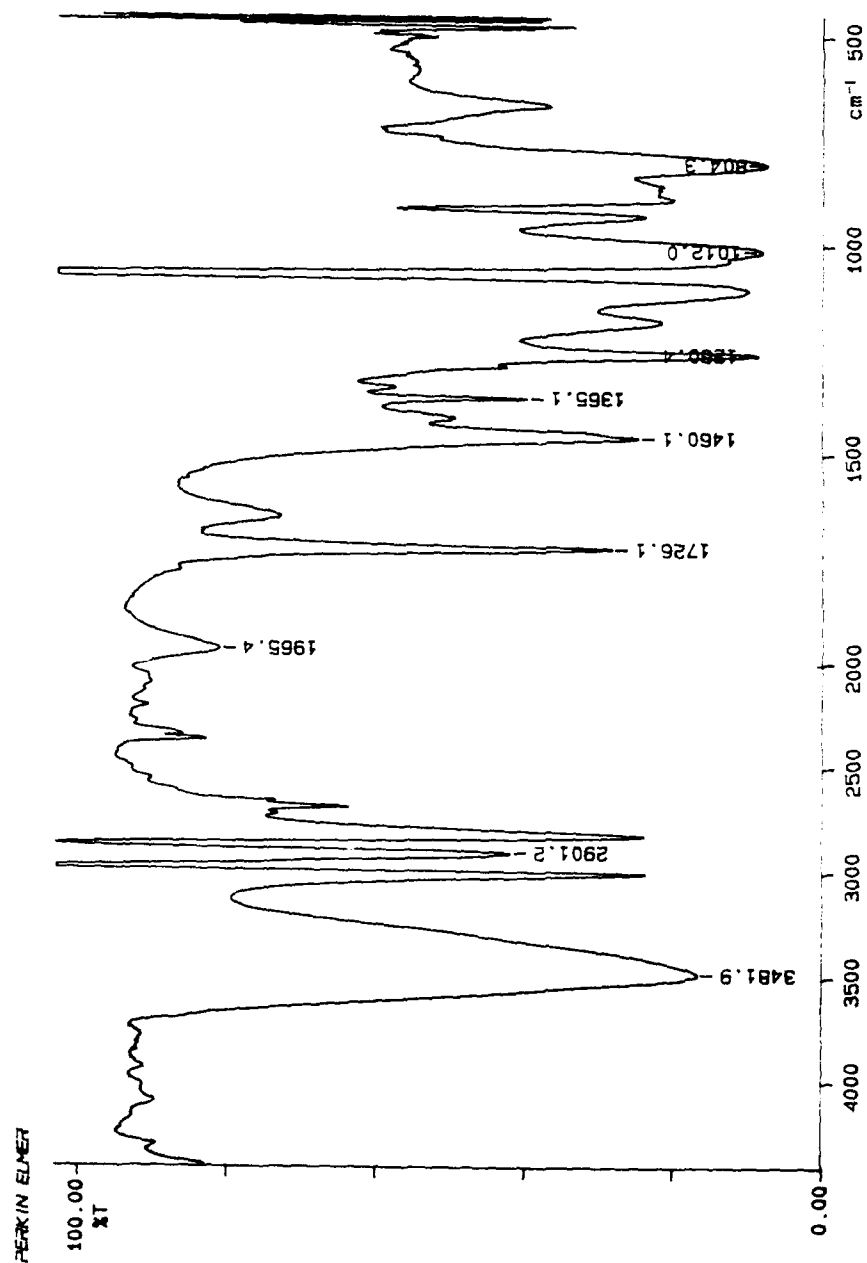
4.1.3 Octenyl Polysiloxane

The octenyl polysiloxane spectrum (Fig. 14) is very similar to the LCP 525 spectrum. Like the LCP spectrum, the Si-H peak is also not present. However, unlike the LCP spectrum, the aromatic ring stretch and the C-O stretch peaks from the LC side chain are not present.

4.1.4 THF Solvents

There were two distinct, unassigned peaks present in all the polymer spectra so far. After confirming that these were not decomposition products of the synthesis, and since these peaks were initially present in the unreacted polysiloxane polymer spectrum, the impurities were deduced to come from the solvent. The spectrum of the stock THF solvent (Fig. 15) supports this; the solvent was contaminated with a carbonyl-containing compound showing a peak at 1726 cm^{-1} , and the peak around 1968 cm^{-1} is most probably an inhibitor added to prevent peroxide formation in the THF.

A new stock THF solvent was opened and used for the LCP X-63 synthesis. The new solvent still shows a peak at 1968 cm^{-1} (Fig. 16).



92/05/09 14: 51
octenpol: 4 scans, 4.0cm-1
octenyl polysiloxane\thf; 5.1% wt

Figure 14. IR spectrum of poly(dimethylsiloxane-co-methyloctenylsiloxane) polymer

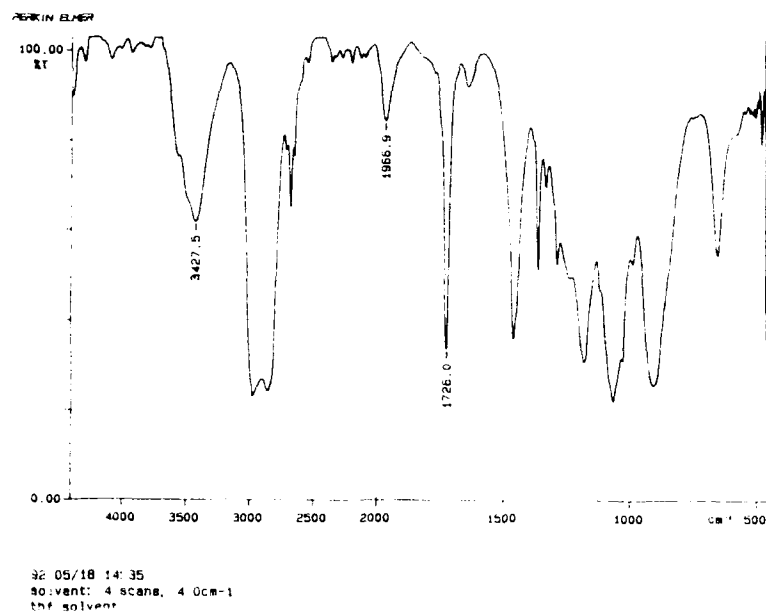


Figure 15. IR spectrum of THF solvent 1

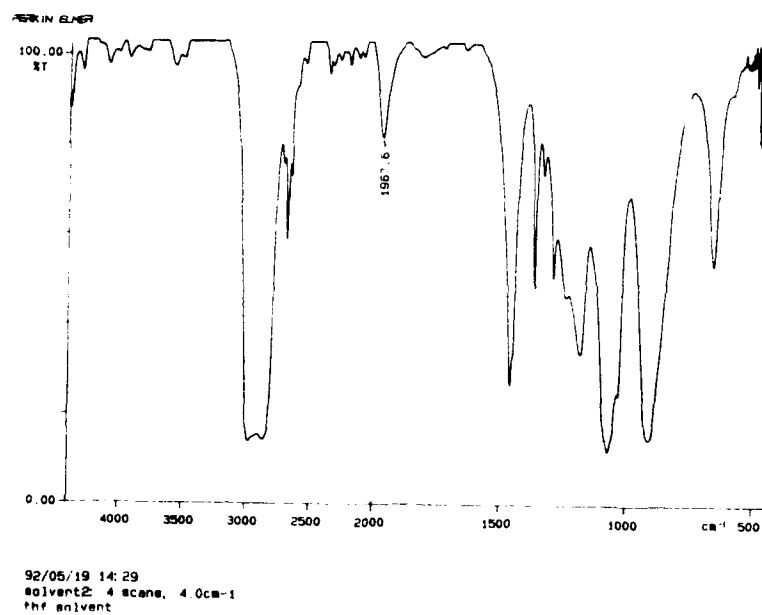


Figure 16. IR spectrum of THF solvent 2

4.1.5 PDMSHMS Polymer (Silicone Fluid X-63)

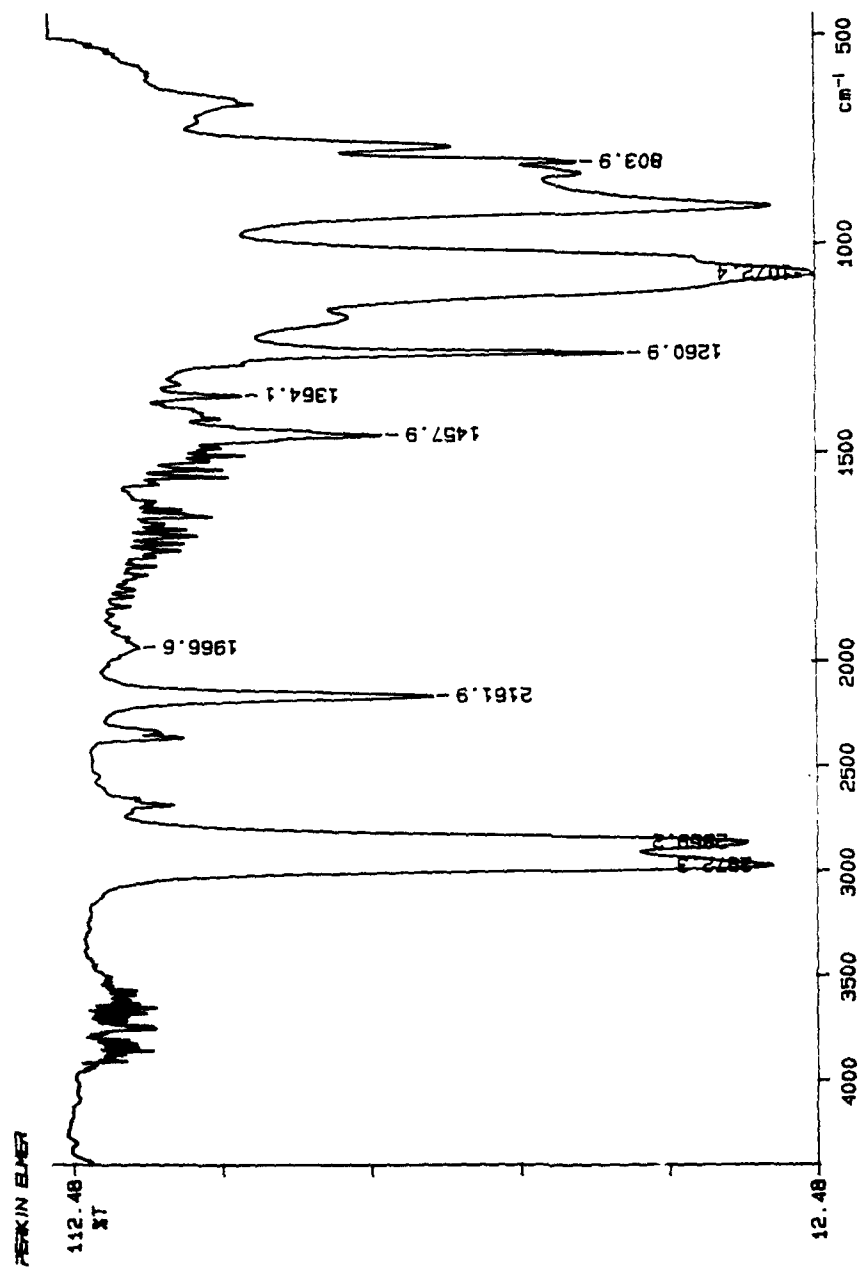
The IR spectrum of the unreacted Silicone Fluid X-63 (Fig. 17) shows the C-H stretches around 2900 cm^{-1} , Si-H stretch at 2162 cm^{-1} , the CH_3 bending peaks at 1458 cm^{-1} and 1364 cm^{-1} , Si- CH_3 rock at 1261 cm^{-1} , Si-O stretch around 1072 cm^{-1} and Si-C stretch at 804 cm^{-1} .

4.1.6 LCP X-63

The IR spectrum of LCP X-63 (Fig. 18) confirms the addition of the LC side chain to the PDMSHMS polymer. Water and methanol residuals are again present around 3480 cm^{-1} . The Si-H absorption peak at 2162 cm^{-1} has disappeared. In addition, the LCP spectrum also shows a C=O stretch at 1736 cm^{-1} , an aromatic ring stretch pair at 1606 cm^{-1} and 1509 cm^{-1} , and the C-O stretch pair around 1180 cm^{-1} . The absorption peak at 1967 cm^{-1} is from the solvent impurity (Fig. 16).

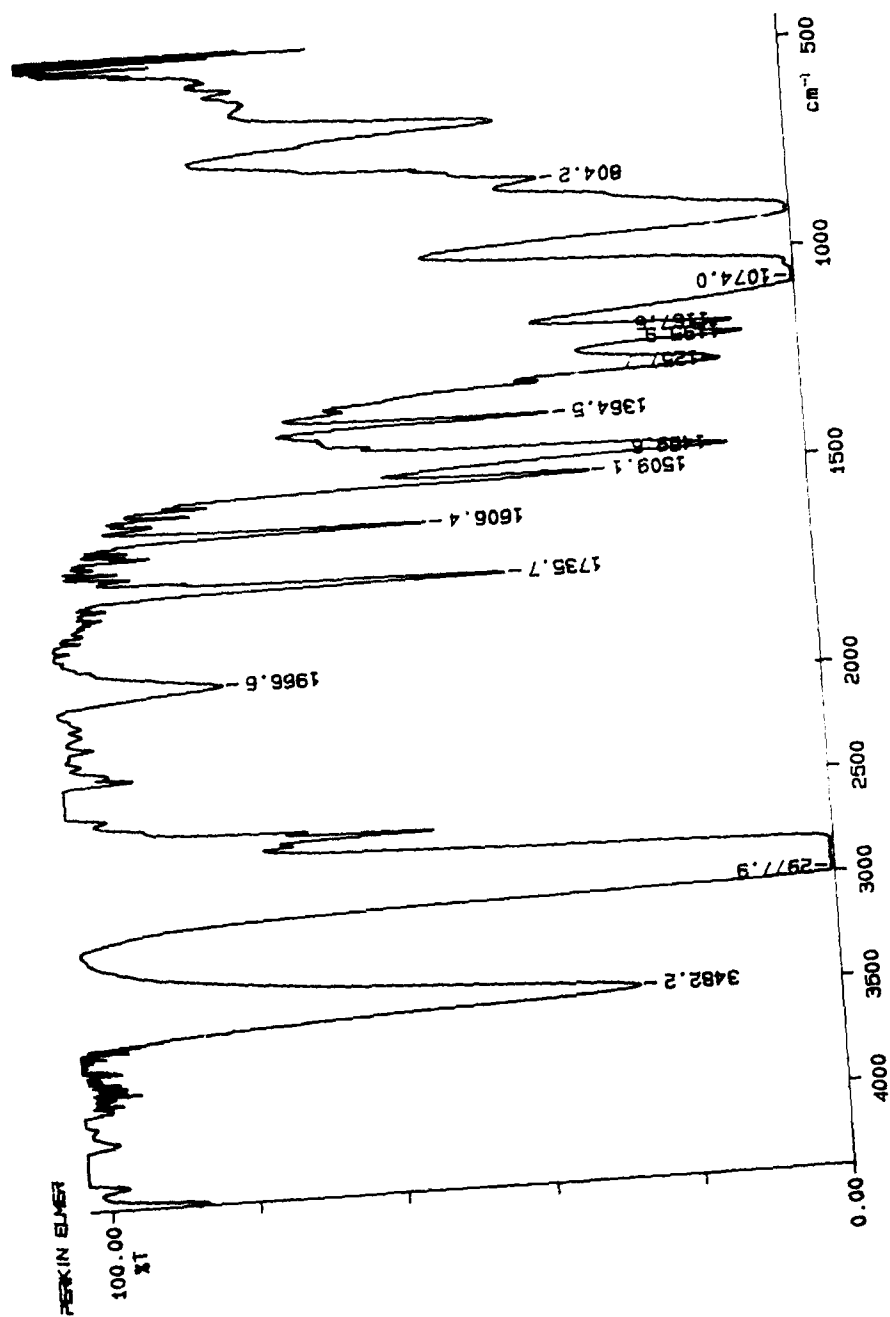
4.2 LCP 525 Films

Shear test was done on two film coatings of different thickness. Film thickness was based on the percent weight



92/05/25 15:05
Y: 4 scans, 4.0cm-1, smooth
x_63\thf; 5.1% wt

Figure 17. IR spectrum of the Silicone Fluid X-63 polymer



92/05/23 17:26
lcp8: 4 scans, 4.0cm-1
lcp8\thf; 5.2% wt

Figure 18. IR spectrum of LCP X-63

of LCP dissolved in the solvent assuming other variables (e.g., amount sprayed, spraying procedure, etc.) were constant.

4.2.1 3.6% Weight LCP 525 Film

For this test, a 2.0 OD neutral density filter was used to prevent light saturation of the camera. Video images of the "wind-off" and "wind-on" conditions were captured as depicted in Figs. 19 and 20, respectively. The wind was blown from left to right. Even though the changes in the raw images are visually undetectable, Fig. 21 shows a difference between the two images; this is the film response due to the applied shear.

Since the background of the two images are similar, the difference between the two image backgrounds would have a gray scale value close to zero, in this case a random noise equal to 0 ± 2 . Since negative numbers lie outside the range of pixel data values (0 to 255), the IPLab software invokes a wrapping feature which process these negative numbers around to become high values, i.e, the new value is equal to the negative number plus 256.²⁴ This creates the speckled pattern of the background random noise. In areas where there was a shear response, the image difference value is positive, albeit a low value, creating a consistent dark



Figure 19. 3.6% weight LCP 525 film "wind-off" image

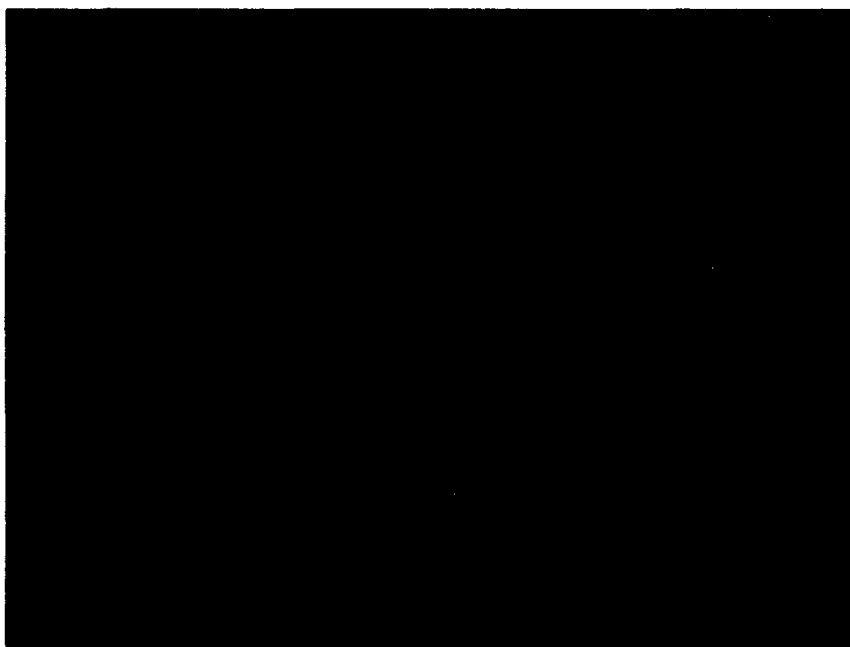


Figure 20. 3.6% weight LCP 525 film "wind-on" image

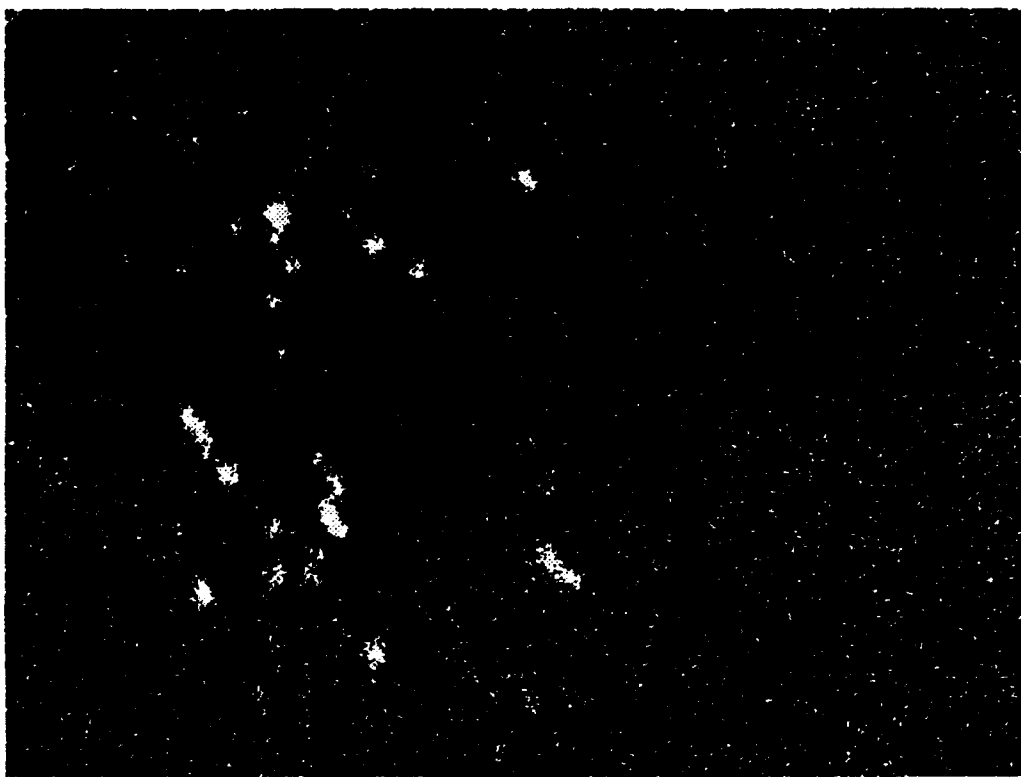


Figure 21. 3.6% weight LCP 525 film shear response; image difference between the "wind-off" and "wind-on" condition

area image. The S/N ratio for this particular film was 5.

The bright spots were the nonuniform bumps on the film which showed greater reorientation response to the applied shear.

Another "wind-off" image was taken, and Fig. 22 shows the difference between the two "wind-off" conditions. There is a slight film deformation, and it is centered around a bump on the film.

Fig. 23 is another image difference due to shear applied. This time wind flowed from slightly lower left to upper right of the plate. The shear response S/N ratio was 4.

4.2.2 4.8% Weight LCP 525 Film

The neutral density filter was scaled down to 0.8 OD and the polarizers slightly uncrossed to increase the transmitted light and, thereby, improve the image signal. The LCP showed a similar response with the slightly thicker film coating. Figs. 24 and 25 are the "wind-off" and "wind-on" condition images, respectively. Image difference in Fig. 26 shows the film's shear response; the S/N ratio increased significantly to 13.5 (27/2).

As observed, the image response comes out bright, vice the dark image response of the 3.6% weight film (Fig. 21).

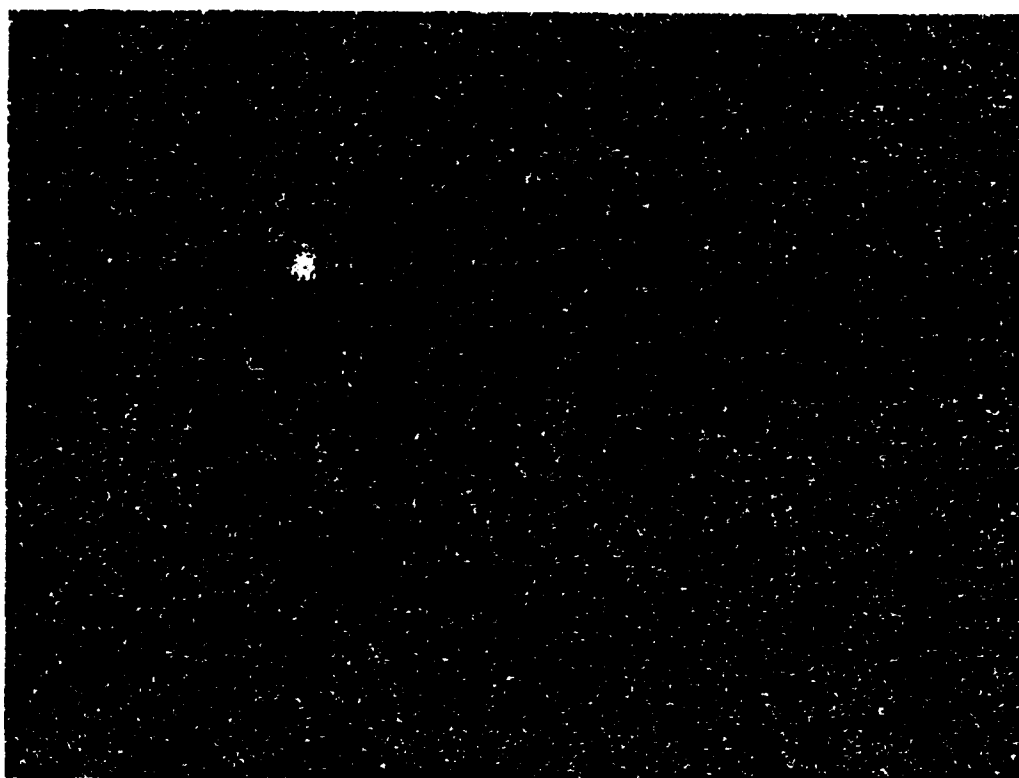


Figure 22. 3.6% weight LCP 525 film deformation due to applied shear; image difference between two "wind-off" conditions, one before and one after shear application

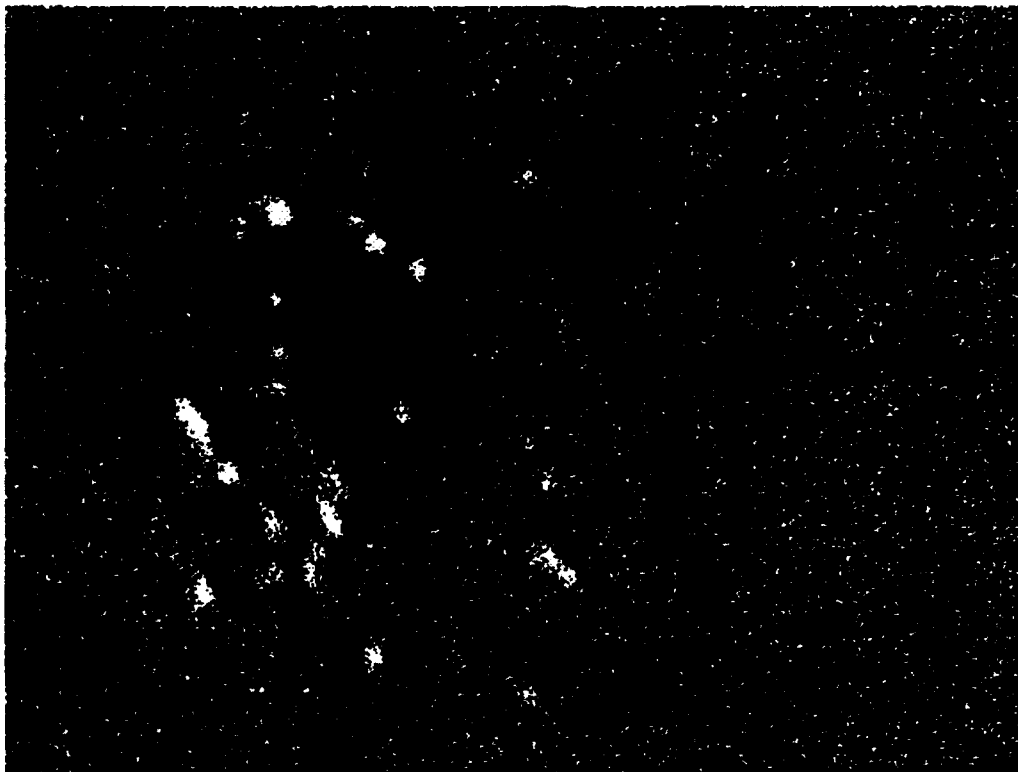


Figure 23. 3.6% weight LCP 525 film shear response; 2nd test; image difference between a "wind-off" and "wind-on" condition

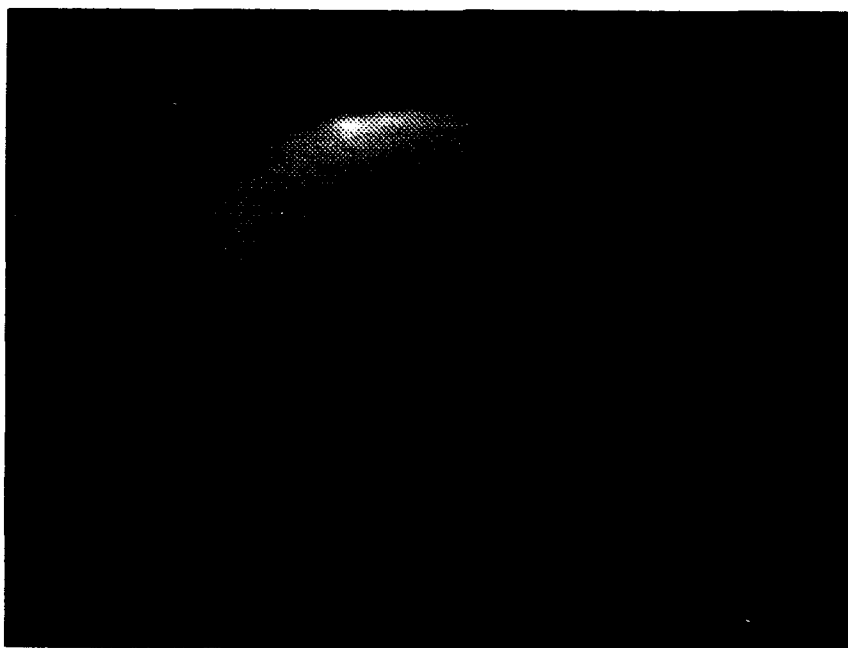


Figure 24. 4.8% weight LCP 525 film "wind-off" image

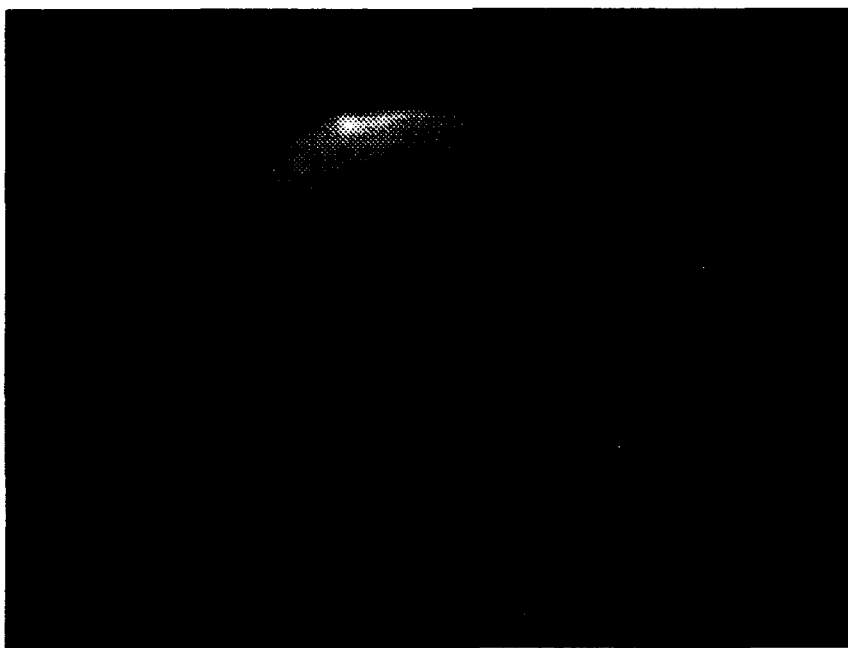


Figure 25. 4.8% weight LCP 525 film "wind-on" image

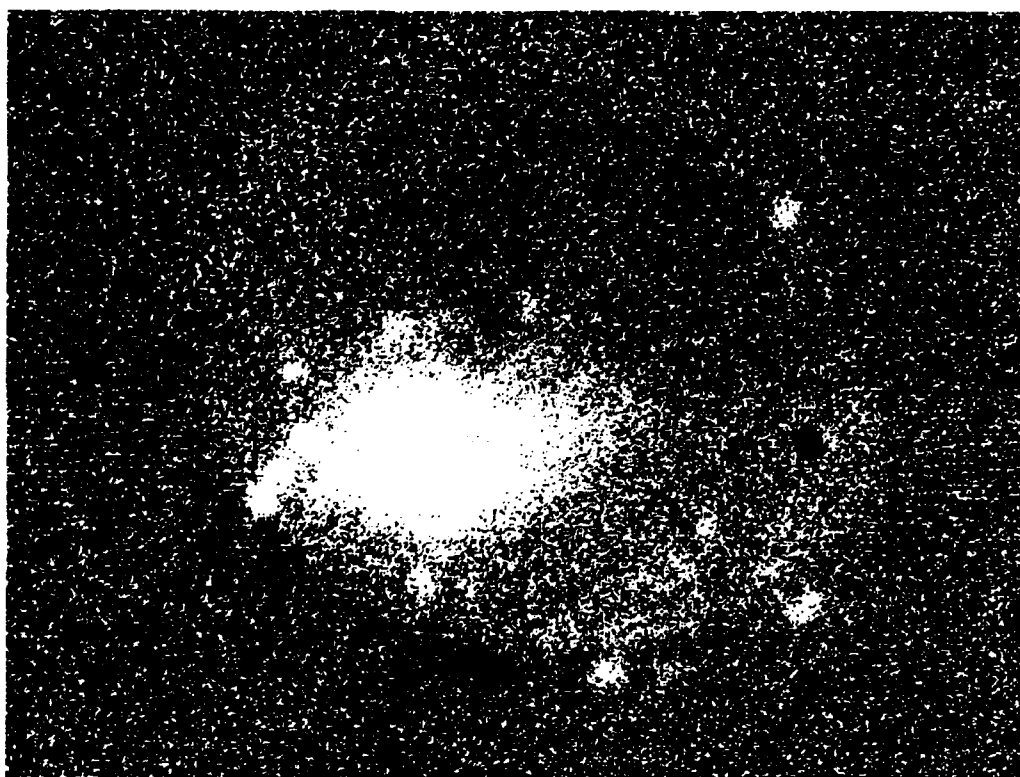


Figure 26. 4.8% weight LCP 525 film shear response; image difference between the "wind-off" and "wind-on" condition

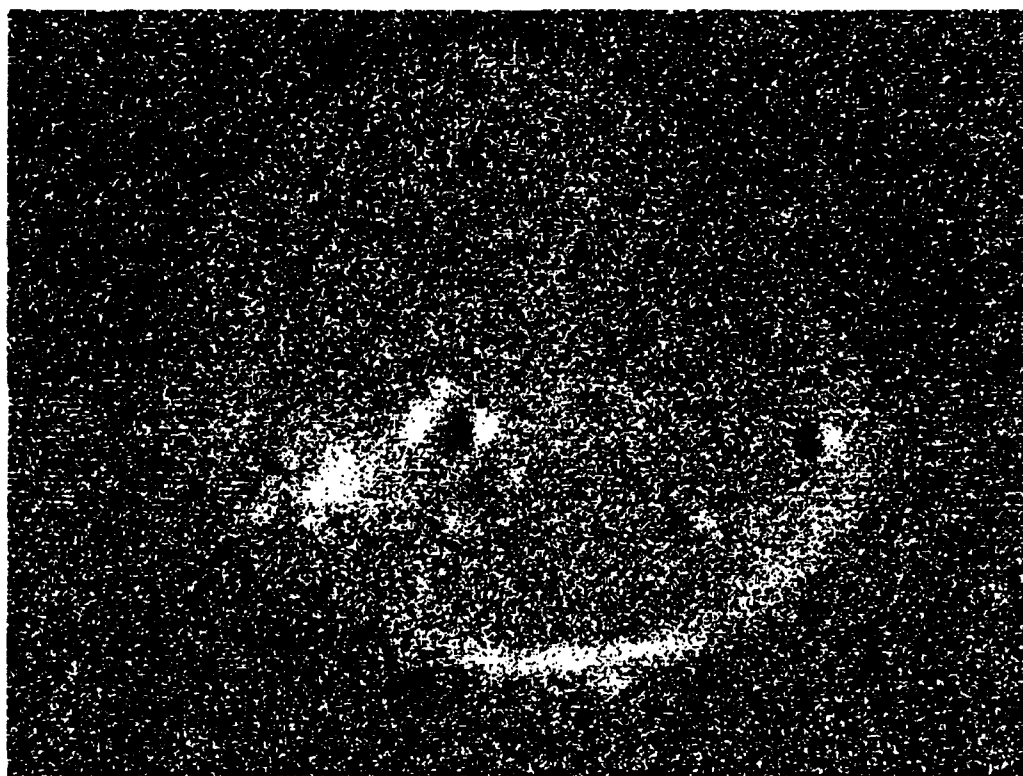


Figure 27. 4.8% weight LCP 525 film deformation due to applied shear; image difference between two "wind-off" conditions, one before and one after shear application

This phenomenon is not really due to film thickness but more due to the uncrossing of the polarizers and the orientation of the LCP relative to the incident polarized light.

Depending on the orientation, the transmitted light becomes brighter or darker upon LCP reorientation when the shear is applied. The image difference in Fig. 27 still shows slight deformation around the nonuniformity on the film.

4.3 Octenyl Polysiloxane Film

A 5.1% weight octenyl polysiloxane coating control was tested to determine if the shear-sensing response is inherent only in side chain LCPs and not just any side chain polymer. 1-octene was chosen because it is similar in length to the LC side chain.

The neutral density filters were left at 0.8 OD with the polarizers slightly uncrossed; light saturation occurred at the bottom of the images. Figs. 28 and 29 are the "wind-off" and "wind-on" images, respectively; the wind was blown from left to right. Fig. 30 is the image difference when shear was applied. As observed, there is no shear response pattern; the image, however, shows deformation around the nonuniformity on the film. Another "wind-off" image was taken, and Fig. 31 is an image difference between the two "wind-off" conditions. There is no difference between

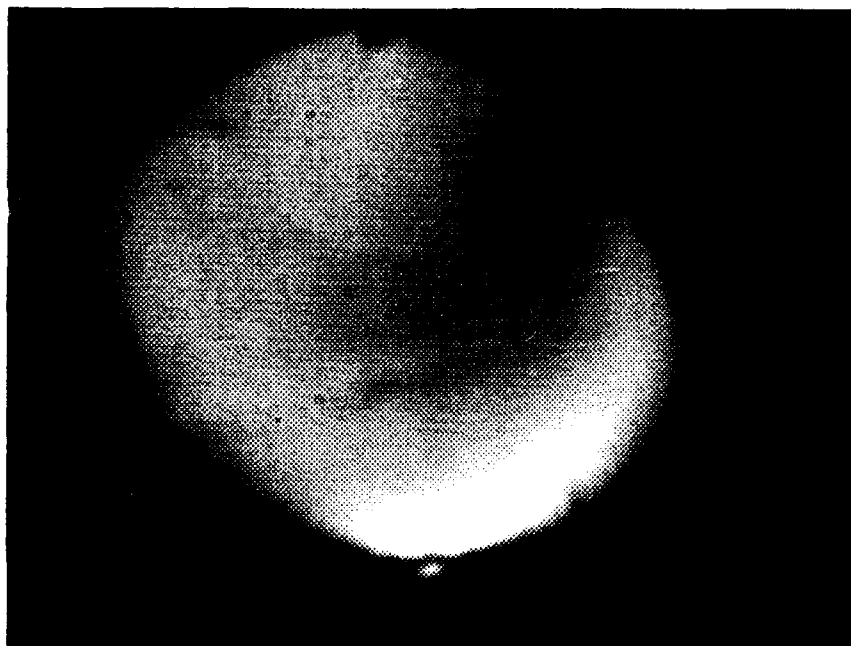


Figure 28. Octenyl polysiloxane film "wind-off" image

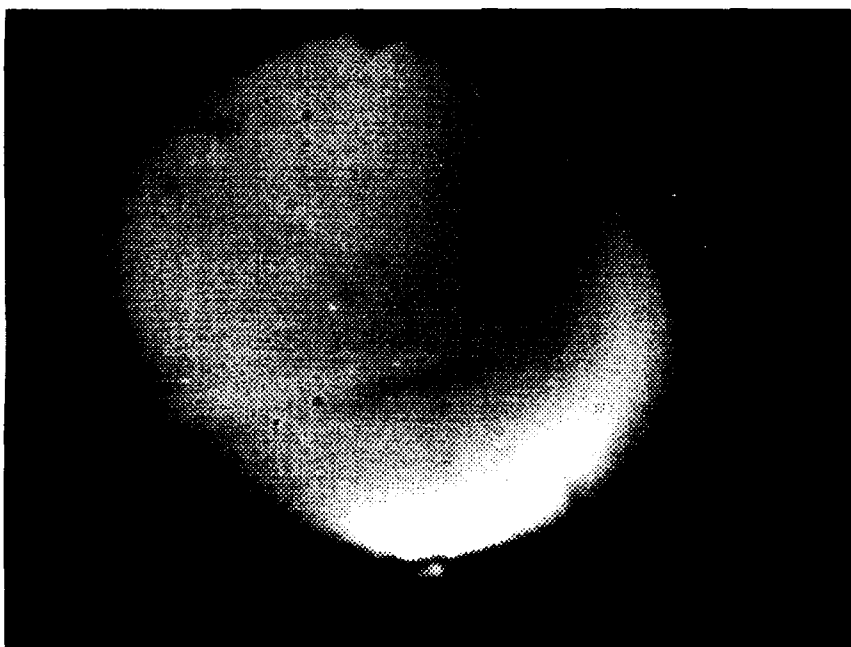


Figure 29. Octenyl polysiloxane film "wind-on" image

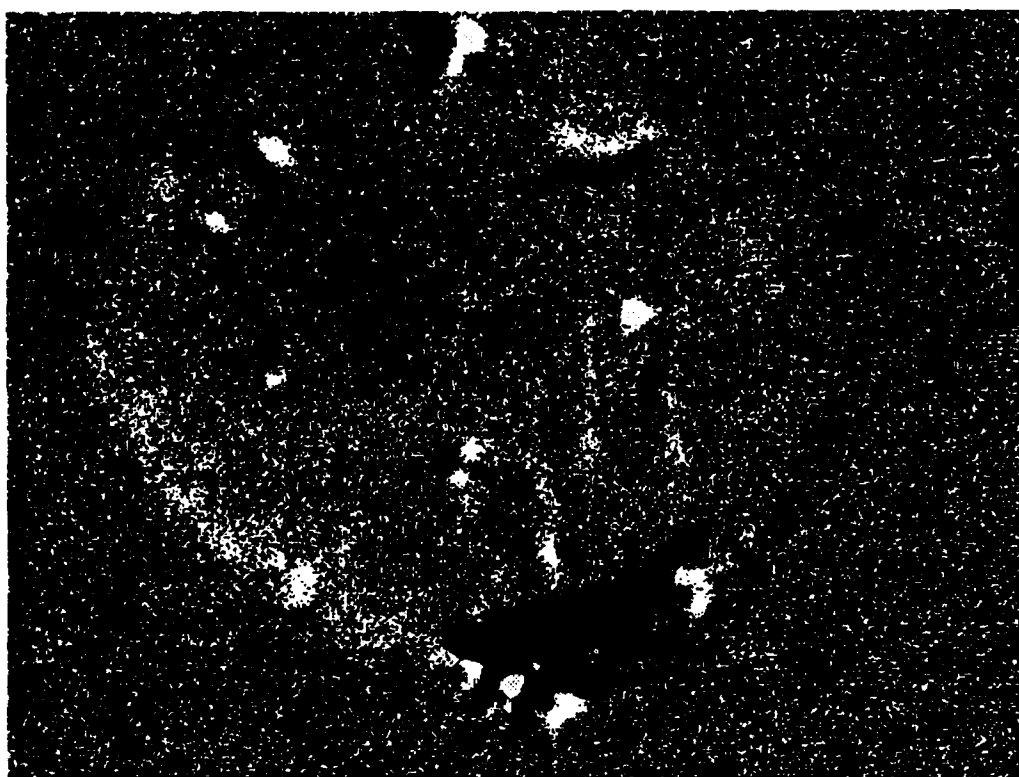


Figure 30. Octenyl polysiloxane film shear response; image difference between the "wind-off" and "wind-on" condition; film shows deformation around the nonuniformity

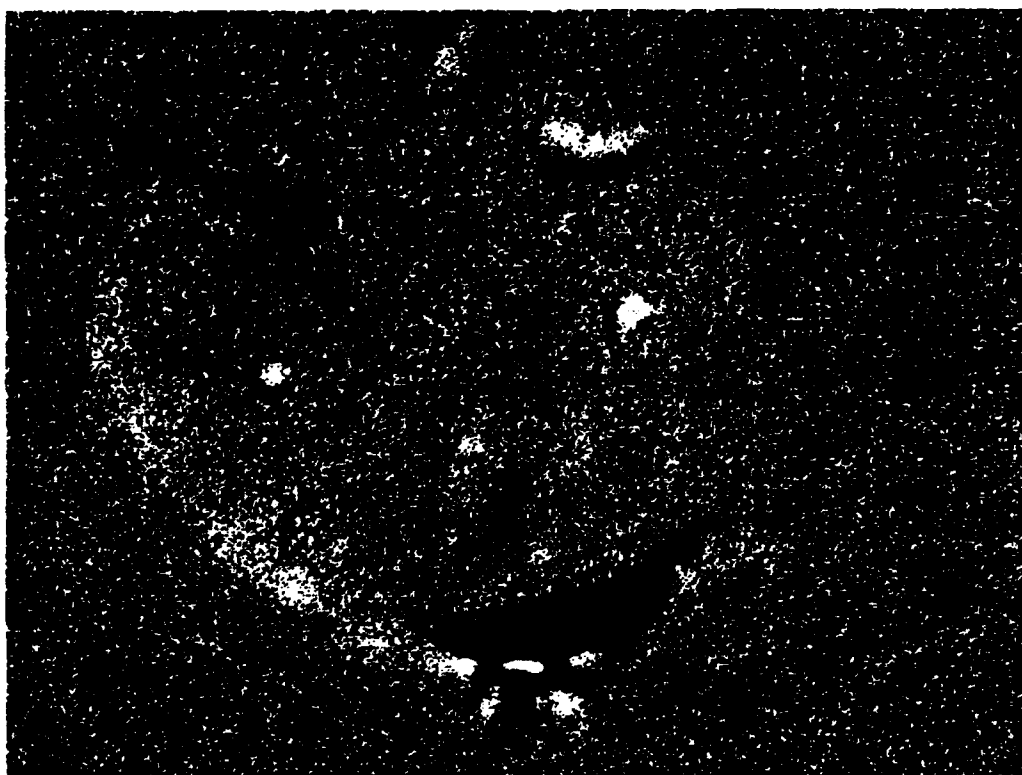


Figure 31. Octenyl polysiloxane film deformation due to applied shear; image difference between two "wind-off" conditions, one before and one after shear application; film shows the same deformation

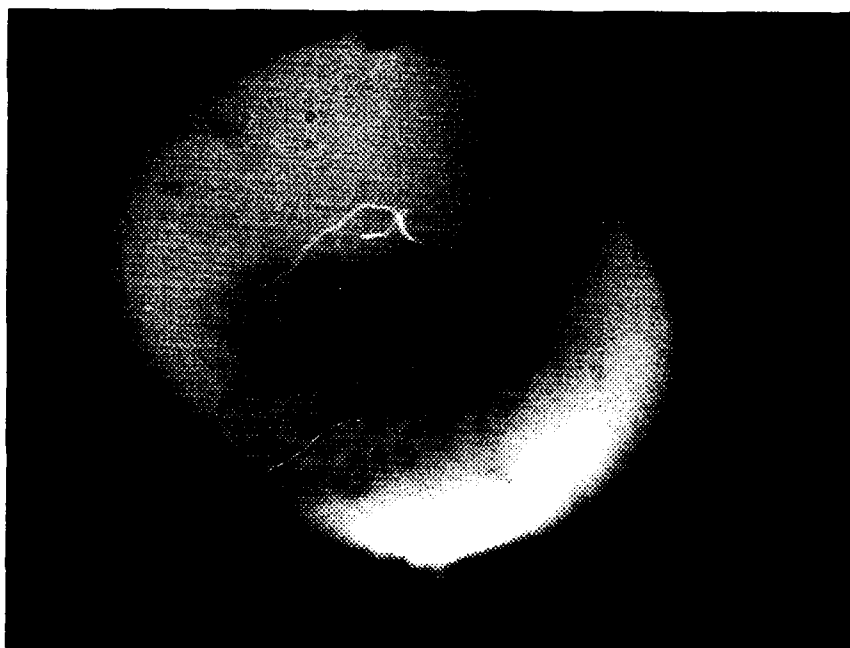


Figure 32. Octenyl polysiloxane film 2nd "wind-on" image; film deforms from increased shear application

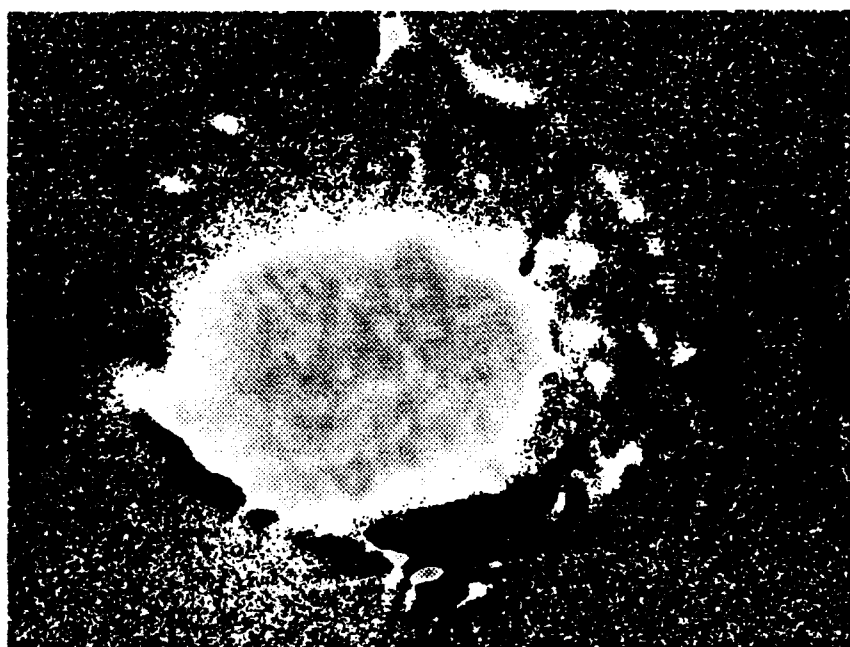


Figure 33. Octenyl polysiloxane film complete deformation due to applied shear; image difference between two "wind-off" conditions, one before and one after shear application

this and the previous image difference; this confirms permanent film deformation due to the applied shear.

The jet nozzle was moved in slightly closer to the plate surface to possibly induce some reorientation response. The film was totally deformed (Figs. 32 and 33); the octenyl polysiloxane coating is not nearly as rigid as the LCP coating.

4.4 LCP X-63 Films

Shear test was done on two 5.2% weight LCP X-63 film coatings. This LCP coating dried to a rougher and more nonuniform surface than the LCP 525 films. This was due to minute amounts of gel byproducts sprayed-on along with the LCP. One of the LCP plates was heated to 85°C (i.e., above T_i) for about 30 minutes with the intent of smoothing out the coating and possibly aligning the LCP orientation upon cooling.

4.4.1 Untreated LCP X-63 Film

The neutral density filters were left at 0.8 OD with the polarizers fully crossed. Figs. 34 and 35 are the "wind-off" and "wind-on" images, respectively; the wind was



Figure 34. Untreated LCP X-63 film "wind-off" image

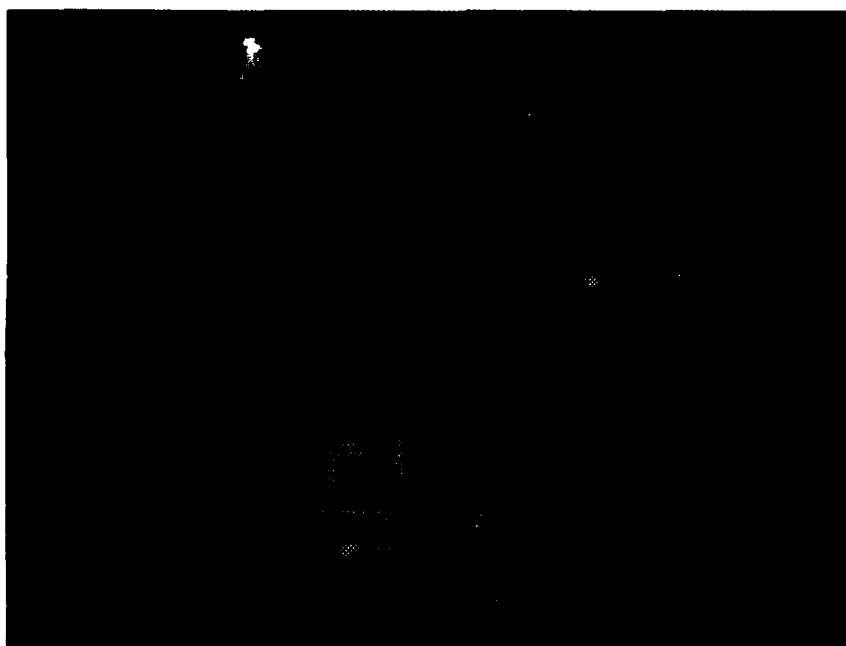


Figure 35. Untreated LCP X-63 film "wind-on" image

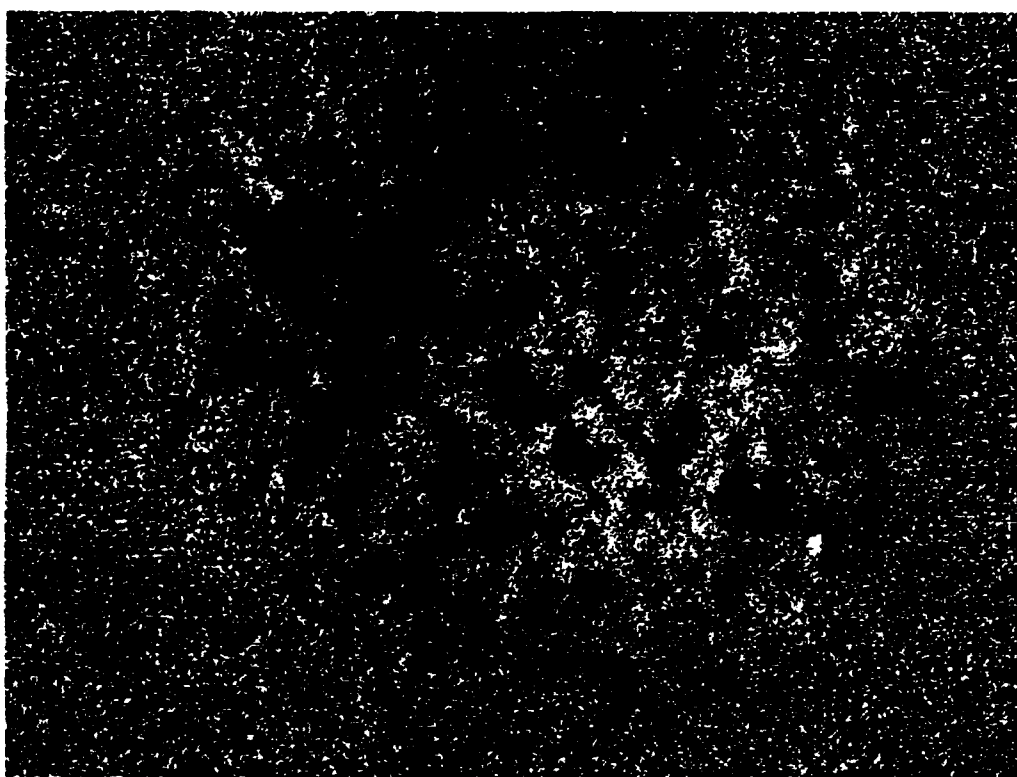


Figure 36. Untreated LCP X-63 film shear response; image difference between the "wind-off" and "wind-on" condition



Figure 37. Untreated LCP X-63 film deformation due to applied shear; image difference between two "wind-off" conditions, one before and one after shear application

blown from left to right. Image difference in Fig. 36 shows the film's shear response; the S/N ratio was 6.5. Another "wind-off" image was taken, and Fig. 37 shows the difference between the two "wind-off" conditions. The image shows slight deformation again around the nonuniformity on the film.

4.4.2 Heat-treated LCP X-63 Film

Figs. 38 and 39 are the "wind-off" and "wind-on" images, respectively; the wind was blown from left to bottom right. The image difference in Fig. 40 shows significant improvement in film response compared to the untreated LCP X-63 film; the S/N ratio increased to 11. Fig. 41 still shows slight deformation due to the applied shear.

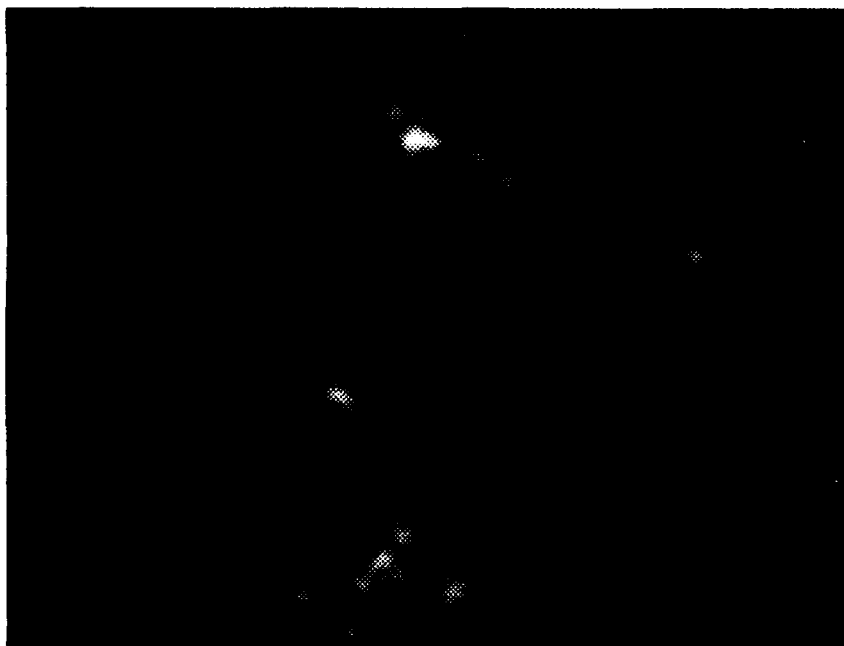


Figure 38. Heat-treated LCP X-63 film "wind-off" image

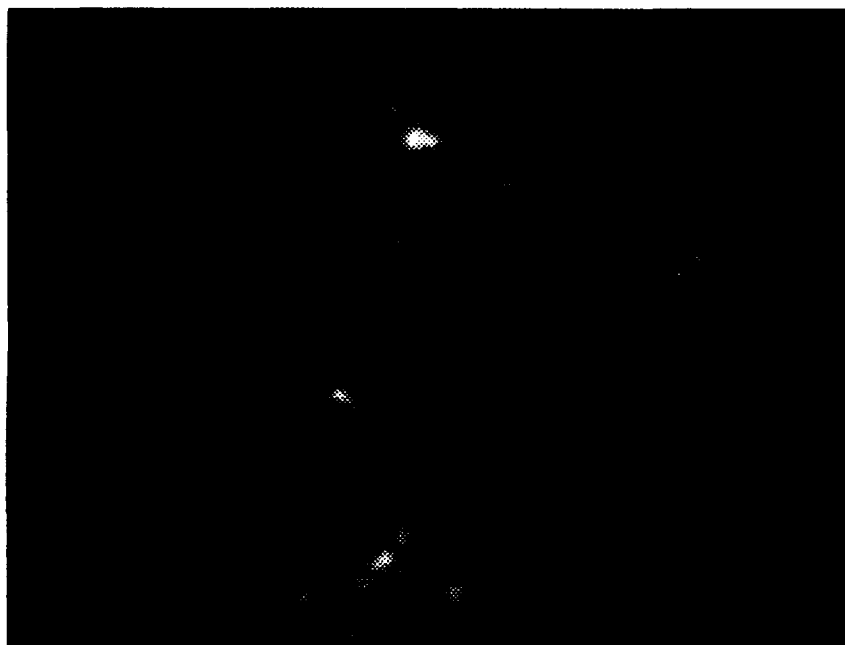


Figure 39. Heat-treated LCP X-63 film "wind-on" image

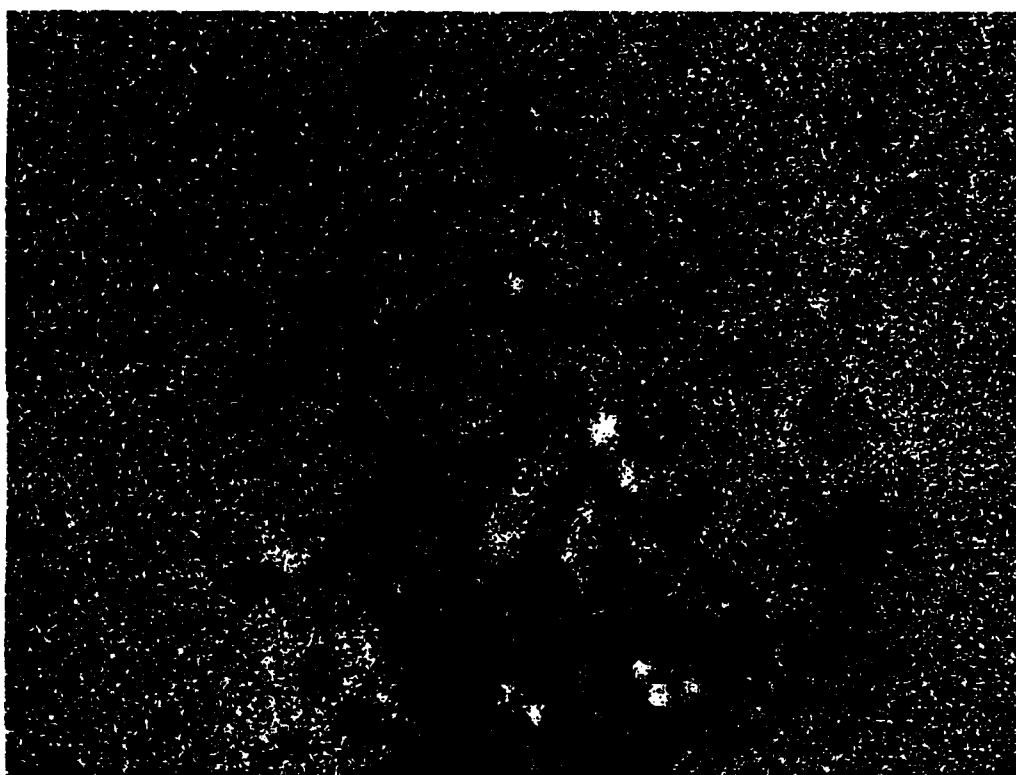


Figure 40. Heat-treated LCP X-63 film shear response; image difference between the "wind-off" and "wind-on" condition

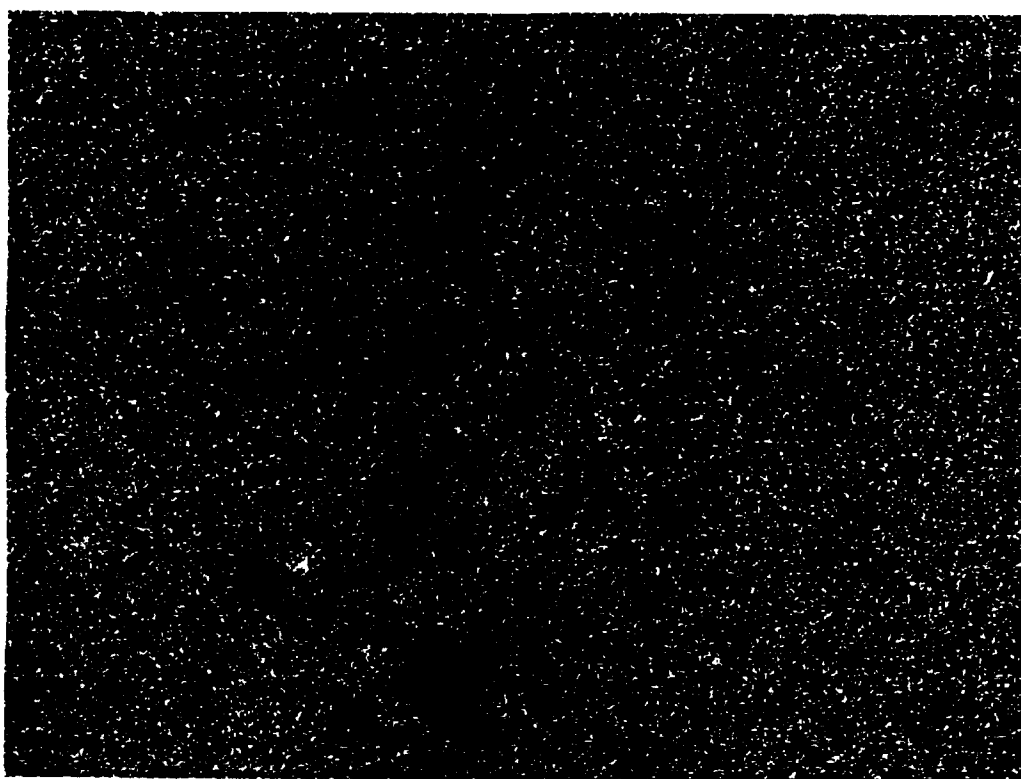


Figure 41. Heat-treated LCP X-63 film deformation due to applied shear; image difference between two "wind-off" conditions, one before and one after shear application

Chapter 5. Conclusion

5.1 Summary of Results

This thesis extends on earlier research on side chain LCPs with low T_g s for a novel application; the study determined the feasibility of using these materials as aerodynamic shear sensors. Different materials were synthesized, spray-coated, treated and tested for their shear-sensing potential.

Although the shear stress applied on the plates was never quantified in this study, the variables for shear application between tests were kept constant as much as possible. The following summarizes the empirical observations of the tests:

1. LCP coatings respond to applied shear. Shear stress produce marked changes in the LCP optical properties, specifically birefringence, and this can be exploited to sense and possibly measure the applied shear.
2. The shear-sensing response is inherent only in LCPs, vice any side chain polymer. The optical behavior observed derives from the mesogenic side chain and partially from the polymer main chain.
3. The noticeable improvement in 4.8% weight LCP 525 film shear response may be due to the increase in film thickness,

but is more likely due to an increase in the incident light illuminating the film. Improved shear responses were also noted on the LCP X-63 films where the neutral density filter was scaled down to 0.8 OD.

4. Heat-treatment significantly improved LCP shear response. This is most likely due to a realignment of the LCP orientation, especially in cases where nonuniformity in the surface might induce lesser LCP orientation.

5. Finally, although not really quantified, film shear response is related to its viscosity. At similar film thickness, the more viscous LCP X-63 film was less responsive than the LCP 525 film. Although there is also the contribution from the large nonuniformity in the LCP X-63 film, higher viscosity induce lesser mesogenic reorientation during shear application which equates to a lesser film response.

5.2 Follow-on Studies

This research merely initiated birefringence study of applied shear on LCP coatings and determined the feasibility of such measurements. Considerably more development work are needed to bring this method into general use:

1. The shear stress applied needs quantitation to calibrate the LCP film response. One option is to construct a

Poiseuille flow channel as depicted in Fig. 42. In this setup, shear applied on the sample plate is determined from the channel height, the pressure gradient and the position in the plate.^{25,26} The next option is to calibrate in a wind tunnel test and compare the results to data taken with current wing shear sensors.

3. Slight film deformation due to the applied shear occurred even with the more viscous LCP X-63. Synthesizing with an even more viscous polymer main chain, e.g., an X:Y ratio of 1:1, might solve this problem. Another option is to work with polyacrylates which are less flexible than polysiloxanes but can still be synthesized to LCPs with low T_g s.¹¹ However, the study should consider the trade-off between viscosity and film shear response.

4. Once an appropriate LCP is selected, the next step is to attach fluorescent probes into the polymer to possibly increase signal response. For the current LCPs, one possible probe is Acrylodan (A-433, Molecular Probes, Inc.) (Fig. 43). This dye is quite suitable because it is similar in structure to the mesogenic side group, thereby, preventing any large disorientation of the mesogens. The dye also includes the terminal double bond required for LCC copolymerization. The study should look at low dye concentrations to limit the change in liquid crystalline behavior^{11,12} and prevent fluorescence autoquenching. The study should also determine the LCC's possible sensitivity

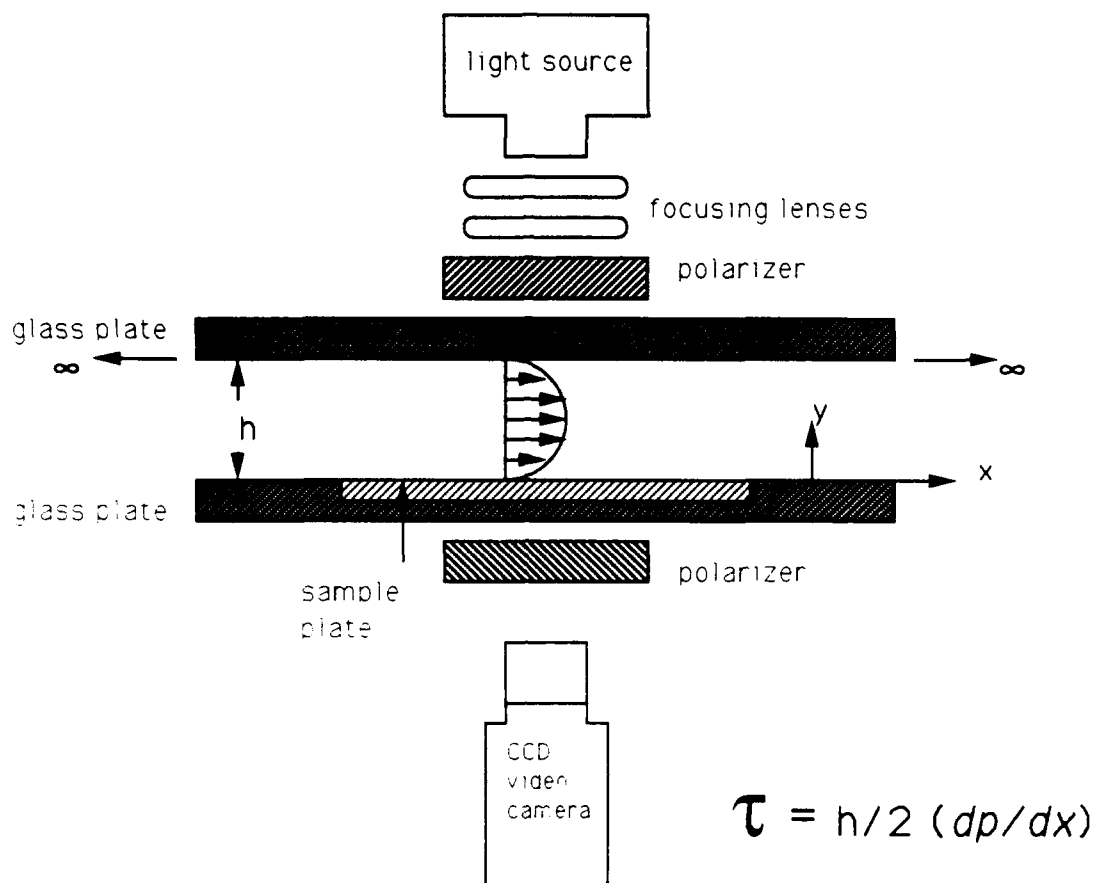


Figure 42. Schematic diagram of a Poiseuille flow channel setup; the channel is infinitely long and wide relative to the height

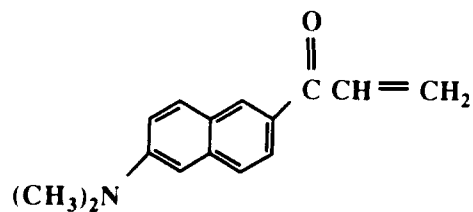


Figure 43. 6-acryloyl-2-dimethylaminonaphthalene (Acrylodan)

to temperature and susceptibility to oxygen quenching.

This thesis was limited by the time constraints of the AFIT master's program. Most of the data results taken were more qualitative in nature. However, the study did confirm the feasibility of measuring shear stress using LCP coatings. Follow-on studies should concentrate on developing this method for practical use in aerodynamic testing.

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